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GENERAL INFORMATION

THE VOLUMETRIC ANALYSIS OF PHOSPHATES

A method has been developed for the volumetric determination of orthophosphate, and a simple variation permits the determination of the average number of phosphorus atoms per molecule in condensed phosphates. For total P_2O_5 the phosphates are converted to the diacid ortho-salt and precipitated as silver phosphate. The liberated acid is then titrated. For determination of chain length the condensed phosphate is converted to the diacid form and treated similarly, then hydrolysed and determined as orthophosphate. The ratio of the two titrations is equal to the average number of phosphorus atoms per molecule.

CATALYSTS FOR CERIUM(IV) OXIDIMETRY

DETERMINATION OF PHOSPHITE, HYPOPHOSPHITE, TELLURIUM AND MERCURY

A new catalytic oxidation procedure, involving the use of a cerium(IV) sulfate reagent in perchloric acid with a mixed silver(I)–manganese(II) perchlorate catalyst, has been developed for the determination of phosphite, hypophosphite, and tellurium. By this method 15–100 mg of phosphite, 5–35 mg of hypophosphite, and 10–105 mg of tellurium may be determined with standard deviations of ± 0.17, ± 0.32, and $\pm 0.21\%$ respectively. A direct titration procedure for mercury(I) is described using a ceric perchlorate solution as titrant with the mixed catalyst system. Samples from 65–510 mg may be analyzed with a standard deviation of $\pm 0.36\%$.

A COMPLEXOMETRIC TITRATION OF INORGANIC SULPHATE IN SYNTHETIC DETERGENTS

An accurate method for the determination of inorganic sulphate in synthetic detergents has been developed. After addition of a cationic surface-active agent (cetyl pyridinium chloride) to an anionic detergent, sulphate can be determined by means of indirect titration with EDTA, using a mixture of Metalphthalein and Naphthol Green B as indicator.

THERMOGRAVIMETRIC DETERMINATION OF MAGNESIUM, POTASSIUM AND LEAD BY PRECIPITATION WITH DILITURIC ACID

The thermolysis curves of magnesium, potassium, and lead diliturate have established that either the hydrated or anhydrous forms of these precipitates are stable enough for their gravimetric use to be possible. Magnesium and lead were determined by precipitation with dilituric acid while potassium was precipitated with trimethylamine diliturate.

THE IDENTIFICATION OF ALIPHATIC AMINES IN AIR AS THEIR BENZAMIDES BY PAPER CHROMATOGRAPHY

A method is described for the separation of amines as their benzamides by paper chromatography. Data are given on separations in two systems. Homologous benzamides from C_1 to C_{10} are best separated on S & S 2040a paper while C_{10} and C_{12} are separated on 2045a paper. When radiocarbon labelled benzamides were chromatographed and placed on x-ray film for eight to ten days with subsequent development of the radioautograph, the lower limit of identification was found to be *ca.* 2.5 μg of each benzamide. The results of analysis for amines in two samples of air particulate matter, and one of atmospheric vapors are presented.

SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM(II) WITH 5(*p*-DIMETHYLAMINOBENZYLIDENE)RHODANINE

A sensitive spectrophotometric method has been developed for the determination of palladium, using 5(*p*-dimethylaminobenzylidene)rhodanine reagent in formic, hydrochloric, or propionic acid solution. The systems conform to Beer's law. The specific absorptivity is in the range 0.38 to 0.40 per p.p.m.–cm in the different solvents. The optimum range for 1.00-cm optical path is about 0.4 to 2.5 p.p.m. of palladium. At higher concentrations of palladium a violet-red precipitate forms within a few minutes. In propionic acid solution maximum color is attained at room temperature in 10 to 15 min, and is stable for more than two hours. The system is somewhat sensitive to hydrogen ion concentration; maximum absorbance and stability are attained at 0.01 N hydrochloric acid in the final solution. Platinum(IV), ruthenium(III), iridium(III), iron(III), chromium(VI), and copper(II) interfere if present in amounts several times greater than the amount of palladium; gold(III) interferes very extensively. The mole ratio method, the continuous variations method, and the slope ratio method all show the mole ratio of DMABR to palladium to be 2 : 1 in the color-forming reaction.

IDENTIFICATION OF PHOSPHATE ANIONS IN NIOBIUM AND TANTALUM PHOSPHATES BY MEANS OF INFRA-RED SPECTRA

Some niobium and tantalum phosphates have been prepared and their infra-red spectra have been recorded and compared with those of reference substances. It has been possible to identify PO_4^{-3}, $P_2O_7^{-4}$ and possibly $P_3O_{10}^{-5}$ groups in different samples of niobium and tantalum phosphates.

MECHANISM OF ELEMENTAL SPECTRAL EXCITATION IN FLAME PHOTOMETRY

It is generally believed that emission spectra result from thermal excitation. It is proposed that ultraviolet light present in a flame is also responsible for exciting metal atoms present. Experimentally it has been shown that the intensity of metal emission spectra is a function of the U.V. characteristics of the flame even at constant flame temperature. It was also demonstrated that spectral intensity can be enhanced by external radiation of U.V. light of the correct wavelength.

SPECTROPHOTOMETRIC STUDY OF THE BERYLLIUM–THORIN COMPLEX AND ITS APPLICATION TO THE DETERMINATION OF BERYLLIUM IN ALLOYS

A spectrophotometric study of the beryllium complex with purified thorin shows the formation of a 1 : 1 complex at pH 12. The dissociation constant obtained after successive corrections for reagent absorbance is $1.38 \cdot 10^{-7}$. Beryllium in concentrations of 0.05% to 2.0% in copper base, zinc base, aluminium base and ferrous alloys can be determined by the formation of the thorin complex after its preliminary separation as acetylacetonate in presence of EDTA.

SPECTROPHOTOMETRIC DETERMINATION OF NIOBIUM WITH ASCORBIC ACID
(in German)

A method is described for the spectrophotometric determination of niobium, with ascorbic acid as reagent. A yellow colour is formed with an extinction maximum at 345 mμ.

APPLICATION OF THE CHRONO-AMPEROMETRY BY ANODIC REDISSOLUTION IN THE DETERMINATION OF TRACES OF TRIPHENYL TIN ACETATE
(in French)

Using a hanging dropping mercury electrode (according to Vogel) the authors find a better sensitivity of measurements in the determination of triphenyl tin acetate as fungicide residues on vegetable matter.

AMPEROMETRIC ARGENTIMETRIC AND MERCURIMETRIC TITRATION OF SULFHYDRYL

II. MERCURIMETRIC TITRATION

The ampero-mercurimetric titration of cysteine (RSH), glutathione (GSH), thioglycolic acid (TSH) and 2-mercaptoethanol (ESH) at the RMPE at pH 9 yields a sharply defined end-point corresponding to the composition $(XS)_2Hg$. Under the same conditions with the RPtWE two breaks are observed in the titration lines with RSH and GSH, corresponding to compositions $(RS)_2Hg$ and $(RS)_2Hg_2$ respectively. On the other hand, with TSH and ESH only one clear break is found at the RPtWE corresponding to $(TS)_2Hg$ or $(ES)_2Hg$. Conditions have been described for the accurate mercurimetric titration of the thiol compounds at pH 2 in the presence of $0.01\ M$ sulfur dioxide at the RMPE. Use of this can be made in the determination of disulfides and in the determination of the equilibrium concentrations of the reaction between a disulfide and a sulfite at varying pH.

SPECTROPHOTOMETRIC DETERMINATION OF ALUMINIUM WITH STILBAZO

The use of stilbazo as a spectrophotometric reagent for aluminium has been investigated. The reagent forms a stable coloured complex with aluminium showing an absorption maximum at 500 mμ. The system obeys Beer's law from 0.1–0.8 p.p.m. aluminium. The molar extinction coefficient and the stoichiometric composition of the coloured complex have been determined.

THE VOLUMETRIC ANALYSIS OF PHOSPHATES

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The determination of total P_2O_5 and of borate are important features of the analysis of detergent powders. Until recently we had always done the former by the standard magnesium pyrophosphate method. This method is tedious, and although it has the advantage of removing the phosphate from solution it does not render the borate readily accessible. We decided to try to develop an alternative method for the phosphate, which must be rapid, simple in operation, reliable and accurate, bring about removal of the phosphate and facilitate the subsequent determination of borate on the same solution. The requirement that the method should be rapid meant that it would have to be either colorimetric or volumetric. There are many colorimetric methods, most of which are variants of either DENIGÈS' method[1] in which phosphomolybdic acid is reduced to molybdenum blue, or of the phosphovanadomolybdate method first described by MISSON[2]. These are rapid and accurate, but do nothing towards making the borate more accessible. There are at least two volumetric methods[3,4] based on the precipitation of phosphomolybdate but in both cases the excess reagents would increase the difficulty in the determination of borate. Other volumetric methods include those by THISTLETHWAITE[5] using bismuth, by RANCKE-MADSEN AND KJAER-GARD[6] using cerium and a number of procedures all essentially the same as that described by CALAMARI AND HUBATA[7] which involves titration between two pH values. In addition many authors[8-13] have used the general principle of titrating the acid liberated when mono- or dihydrogen orthophosphates are treated with silver ion. FLATT AND BRUNISHOLZ[14] developed a potentiometric titration with silver which they described as "of limited accuracy" and an alternative method in which the phosphate was precipitated with excess silver. The precipitate was filtered off and the excess silver titrated with thiocyanate.

We attempted this last process independently and found difficulty in ensuring quantitative precipitation of the silver phosphate. Eventually we developed a method in which quantitative precipitation was achieved by titrating the liberated acid. We thus produced a technique essentially like the group of methods[8-13] already mentioned, but differing in some important details. For example, other workers had used various indicators to determine the end-point where we used a pH-meter. The latter gave greatly increased accuracy and showed that the indicators had not always been well-chosen. (We did try using methyl red and bromocresol green, but found that both were adsorbed by the precipitate). Systematic study showed that the new technique was not only rapid, simple and reliable, but also gave excellent precision and permitted the subsequent determination of borate by a sequence of operations

taking only about 15 min. We also observed that if we started with the diacid form, not only orthophosphates but also condensed phosphates would yield two equivalents of titratable hydrogen ion per molecule, and this was utilised in a new method for determining the average number of phosphorus atoms per molecule in condensed phosphates.

<div align="center">PRINCIPLES</div>

For the determination of orthophosphate two reactions are of possible use:

$$Na_2HPO_4 + 3\ AgNO_3 \rightarrow Ag_3PO_4 \downarrow + 2\ NaNO_3 + HNO_3$$

$$NaH_2PO_4 + 3\ AgNO_3 \rightarrow Ag_3PO_4 \downarrow + NaNO_3 + 2\ HNO_3$$
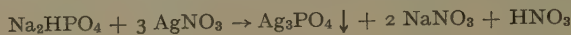
The first of these was used by GERBER AND MILES for the determination of ortho-phosphate in condensed phosphates. The initial pH to which the solution must be adjusted before addition of the silver nitrate is 9.2 in the first case and 4.5 in the second. The end-point in the subsequent titration occurs at a pH of 4.8 in the presence of ammonium ions and at 6.0 in their absence. Interference from salts of weak acids, such as borates and silicates, would therefore be more serious if the monoacid salt were used as the starting material than if the diacid salt were used, and we accordingly chose the latter. In order to minimise such interference most of the experimental titrations were done in the presence of ammonium nitrate. This was found later to be undesirable when borate was to be determined on the same solution, and a series of experiments was performed to show that omission of the ammonium salt did not cause significant error.

It is important to keep the concentration of ammonium ion low, however, as the following experiment showed. The pH of a 5% silver nitrate solution was found to be 5.9 and that of a 20% ammonium nitrate solution 4.8. Equal volumes of the two solutions were mixed together; the pH of the mixture was 3.5. In the absence of any interaction the expected pH would be approximately 5.1. The hydrogen ions responsible for this drop in pH are presumably liberated in the formation of argento-diammine:

$$Ag^+ + 2\ NH_4^+ \rightleftharpoons Ag(NH_3)_2^+ + 2\ H^+$$
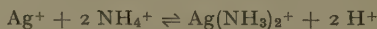
In all the titrations described in this paper the "blank" due to ammonium ions was less than 0.02 ml and was considered negligible.

<div align="center">PROCEDURE</div>

Place a sample containing approximately 1 g or 0.1 g of P_2O_5, present as orthophosphate, in a 400-ml beaker. Insert pH meter electrodes and an electric stirrer. Add 100 ml of water, or more if necessary to immerse the electrodes. With the stirrer running, add 3 N nitric acid if necessary to bring the pH below 4.5. Adjust the pH to lie in the range 4.5 to 4.6 by addition of standard sodium hydroxide. If approximately 1 g of P_2O_5 was taken, use N alkali for this adjustment and the subsequent titration; for the smaller sample use 0.1 N alkali. Add 5 ml of 20% ammonium nitrate if N alkali is being used, or 1 ml if 0.1 N alkali is being used. Finally add the calculated amount of 10% silver nitrate (see below) and titrate with standard sodium hydroxide until the pH lies in the range 4.8 to 4.9.

$$\text{1 ml } N \text{ sodium hydroxide} \quad \equiv 0.0355 \;\; \text{g } P_2O_5$$
$$\text{1 ml 0.1 } N \text{ sodium hydroxide} \equiv 0.00355 \text{ g } P_2O_5$$

The volume of silver nitrate to be used is approximately three times the expected titration for a 1-g sample and one-tenth of this amount for a 0.1-g sample. This should be a sufficient excess, but it is advisable to add a further 5 ml at the end of the titration. More than a fractional drop in the indicated pH shows that insufficient silver nitrate was added.

RESULTS

The method was tested on 0.5 M and 0.05 M solutions of disodium hydrogen phosphate. 10-ml and 25-ml portions were analysed as described, both alone and in the presence of other salts which are commonly found in detergent powders. As a check on the completeness of precipitation the silver phosphate was filtered off, dissolved in 3 N nitric acid and titrated with 0.1 N ammonium thiocyanate using ferric alum as the indicator. In the series using 0.5 M phosphate the solution was diluted to 250 ml and a 25-ml aliquot used for this titration. Note that in the precipitation of one mole of silver phosphate two equivalents of hydrogen ion are liberated but three equivalents of silver ion are consumed. The thiocyanate titration should therefore be 1.5 times as great as the alkali titration.

The figures quoted in the tables of results under the heading "Theoretical titration" were determined by titration with standard acid between pH 9.15 and pH 4.55, these being the determined points of inflexion.

TABLE I

TITRATION OF 10 ml 0.5 M Na_2HPO_4

Foreign salt	Amount of foreign salt	Theoretical titration ml N NaOH	Actual titration ml N NaOH	NH₄CNS titration ml 0.1 N
—	—	10.01	10.01	—
—	—	10.01	10.03	14.88
—	—	10.01	10.05	14.88
—	—	10.01	10.05	14.89
—	—	10.01	10.04	14.89
$NaBO_2$	10 ml 0.1 M	10.01	10.02	14.93
$NaBO_2$	10 ml 0.1 M	10.01	10.02	14.93
$NaBO_2$	10 ml 0.1 M	10.01	10.04	14.90
$NaBO_2$	10 ml M	10.01	10.06	14.88
$NaBO_2$	10 ml M	10.01	10.08	14.86
$NaBO_2$	10 ml M	10.01	10.10	14.90
Na_2SO_4	20 g	8.87	8.86	—
Na_2SO_4	20 g	8.87	8.86	—
Na_2SO_4	20 g	8.87	8.92	—
A.A.S.[a]	2 g	8.87	8.30	unfilterable
A.A.S.[a]	2 g	8.87	8.30	unfilterable
A.A.S.[a]	2 g	8.87	8.28	unfilterable
Na_2SiO_3	1 g	8.87	8.98	—
Na_2SiO_3	1 g	8.87	8.98	—
Na_2SiO_3	1 g	8.87	8.96	—

[a] A.A.S. = sodium alkylaryl sulphonate.

TABLE II

TITRATION OF 25 ml 0.5 M Na$_2$HPO$_4$

Foreign salt	Amount of foreign salt	Theoretical titration ml N NaOH	Actual titration ml N NaOH	NH$_4$CNS titration ml 0.1 N
—	—	25.02	24.98	37.39
—	—	25.02	25.00	37.40
—	—	25.02	25.00	37.40
—	—	25.02	25.00	37.40
NaBO$_2$	25 ml 0.1 M	25.02	25.11	—
NaBO$_2$	25 ml 0.1 M	25.02	25.09	37.40
NaBO$_2$	25 ml 0.1 M	25.02	25.08	37.40
NaBO$_2$	25 ml 0.1 M	25.02	25.10	37.40
NaBO$_2$	25 ml 0.1 M	25.02	25.07	37.40
NaBO$_2$	25 ml M	22.18	22.18	33.18
NaBO$_2$	25 ml M	22.18	22.17	33.20
NaBO$_2$	25 ml M	22.18	22.18	33.20
Na$_2$SO$_4$	50 g	22.18	21.12	34.90
Na$_2$SO$_4$	50 g	22.18	20.74	—
Na$_2$SO$_4$[a]	50 g	22.18	21.70	—
Na$_2$SO$_4$[b]	50 g	22.18	21.87	34.88
Na$_2$SO$_4$[c]	50 g	22.18	22.12	34.80
Na$_2$SO$_4$[c]	50 g	22.18	22.17	34.94
Na$_2$SO$_4$[c]	50 g	22.18	22.16	35.00
Na$_2$SO$_4$[c]	50 g	22.18	22.14	35.03
Na$_2$SO$_4$	20 g	22.18	22.14	33.38
Na$_2$SO$_4$	20 g	22.18	22.12	33.35
Na$_2$SO$_4$	20 g	22.18	22.12	33.35
A.A.S.	5 g	22.18	19.86	unfilterable
A.A.S.[c]	5 g	22.18	22.90	unfilterable
A.A.S.	5 g	22.18	19.88	unfilterable
A.A.S.	1 g	22.18	20.56	unfilterable
A.A.S.	1 g	22.18	20.52	unfilterable
Na$_2$SiO$_3$	1 g	22.18	22.33	—
Na$_2$SiO$_3$	1 g	22.18	22.35	—
Na$_2$SiO$_3$	1 g	22.18	22.33	—
Na$_2$CO$_3$	1 g	22.18	22.35	—
Na$_2$CO$_3$	1 g	22.18	22.35	—

[a] 80 ml of 10% silver nitrate
[b] 90 ml of 10% silver nitrate
[c] 100 ml of 10% silver nitrate
70 ml of 10% silver nitrate was used in all those experiments not marked with superscripts

EFFECT OF OMITTING AMMONIUM NITRATE

A further set of titrations was carried out using 0.5 M and 0.05 M phosphate, to see whether the omission of ammonium nitrate would have an adverse effect. 10-, 25- and 50-ml portions of each solution were analysed by the method described, using 10 ml of 20% ammonium nitrate in each of the experiments with 0.5 M phosphate and 1 ml in each of those with 0.05 M phosphate. These two series were then repeated with the omission of the ammonium nitrate, the final titration now being taken to a pH of 6.0. In the series with 0.5 M phosphate there was no significant difference between the experiments with and without ammonium nitrate, but in the series with 0.05 M

TABLE III

TITRATION OF 10 ml 0.05 M Na$_2$HPO$_4$

Foreign salt	Amount of foreign salt	Theoretical titration ml 0.1 N NaOH	Actual titration ml 0.1 N NaOH	NH$_4$CNS titration ml 0.1 N
—	—	10.00	9.67	14.42
—	—	10.00	9.63	14.42
—	—	10.00	9.63	14.45
NaBO$_2$	10 ml 0.1 M	10.00	9.96	14.98
NaBO$_2$	10 ml 0.1 M	10.00	9.98	14.98
NaBO$_2$	10 ml 0.1 M	10.00	9.96	15.00
Na$_2$SO$_4$	5 g	10.00	9.95	—
Na$_2$SO$_4$	5 g	10.00	9.98	—
Na$_2$SO$_4$	5 g	10.00	9.95	—
Na$_2$SiO$_3$	0.2 g	10.00	9.98	—
Na$_2$SiO$_3$	0.2 g	10.00	10.00	—
Na$_2$SiO$_3$	0.2 g	10.00	9.98	—
Na$_2$CO$_3$	0.1 g	10.00	10.00	—
Na$_2$CO$_3$	0.1 g	10.00	9.97	—

TABLE IV

TITRATION OF 25 ml 0.05 M Na$_2$HPO$_4$

Foreign salt	Amount of foreign salt	Theoretical titration ml 0.1 N NaOH	Actual titration ml 0.1 N NaOH	NH$_4$CNS titration ml 0.1 N
—	—	25.00	24.98	37.40
—	—	25.00	25.00	37.42
—	—	25.00	25.00	37.42
NaBO$_2$	25 ml 0.1 M	25.00	24.98	37.42
NaBO$_2$	25 ml 0.1 M	25.00	25.00	37.40
NaBO$_2$	25 ml 0.1 M	25.00	25.00	37.42
Na$_2$SO$_4$	5 g	25.00	25.00	—
Na$_2$SO$_4$	5 g	25.00	25.00	—
Na$_2$SO$_4$	5 g	25.00	25.01	—
A.A.S.	0.1 g	25.00	24.53	—
Na$_2$SiO$_3$	0.2 g	25.00	25.00	—
Na$_2$SiO$_3$	0.2 g	25.00	24.98	—
Na$_2$SiO$_3$	0.2 g	25.00	25.00	—

phosphate there was a small difference, the titrations without ammonium nitrate being slightly higher. The greatest difference was in the titration of a 50-ml aliquot, where duplicate sets disagreed by 0.24 and 0.27 ml respectively. A blank was run on 50 ml of the 0.1 N sodium hydroxide without ammonium nitrate and gave a titration of 0.19 ml. This is attributed to traces of carbonate in the alkali. A similar blank with ammonium nitrate gave a titration of less than 0.02 ml. The figures in Table V are corrected for these blanks.

A further seven titrations were done using 0.5 M phosphate to which sodium borate, sulphate and silicate were added. The results of this test are shown in Table VI.

It was concluded that even in the presence of other salts the omission of ammonium nitrate made a negligible difference to the result.

Halides interfere only by preferentially precipitating silver. The remedy is to add additional silver nitrate solution equivalent to the halide present.

TABLE V

COMPARISON OF EXPERIMENTS WITH AND WITHOUT AMMONIUM NITRATE

0.5 M Na₂HPO₄			0.05 M Na₂HPO₄		
Volume taken, ml	Titration with NH₄NO₃, ml	Titration without NH₄NO₃, ml	Volume taken, ml	Titration with NH₄NO₃, ml	Titration without NH₄NO₃, ml
10	9.82	9.82	10	9.84	9.84
10	9.80	9.83	10	9.80	9.85
25	24.50	24.56	25	24.55	24.49
25	24.49	24.51	25	24.50	24.49
50	48.85	49.00	50	49.01	49.06
50	48.78	49.02	50	48.96	49.04

TABLE VI

EFFECT OF OTHER SALTS ON TITRATIONS WITHOUT AMMONIUM NITRATE

Foreign salt	Amount of foreign salt	Amount of 0.5 M phosphate (ml)	Theoretical titration (ml N NaOH)	Actual titration (ml N NaOH)
NaBO₂	10 ml 0.1 M	10	9.82	9.86
NaBO₂	10 ml 0.1 M	10	9.82	9.85
NaBO₂	10 ml 0.1 M	10	9.82	9.87
Na₂SO₄	50 g	25	24.57	24.62
Na₂SO₄	20 g	25	24.57	24.55
Na₂SiO₃	1 g	25	24.57	24.50
Na₂SiO₃	1 g	25	24.57	24.58

EFFECT OF SURFACE ACTIVE MATTER

It will be obvious from the results in Tables I, II and IV that the presence of sodium alkylarylsulphonate completely vitiates the determination of phosphate. A set of experiments was done to attempt to establish a tolerance level for this material. In all experiments 25 ml of 0.05% M phosphate, 100 ml of water and 10 ml of 10% silver nitrate were used. Successively increasing amounts of 1% sodium alkylarylsulphonate solution were added and the results noted. In the absence of ammonium nitrate up to 0.02 g of the surface active material made no significant difference. With 0.03 g the error was only 0.12 ml. With 0.04 g the error was 0.45 ml and became rapidly greater with increasing contamination, reaching 4.4 ml with 0.1 g of surface active matter. All these erroneous results were too high.

With 1 ml of 20% ammonium nitrate there was again no error up to 0.02 g of contamination. The error then increased rather more rapidly than before, reaching 5.8 ml with 0.1 g of surface active matter. All these erroneous results were too low.

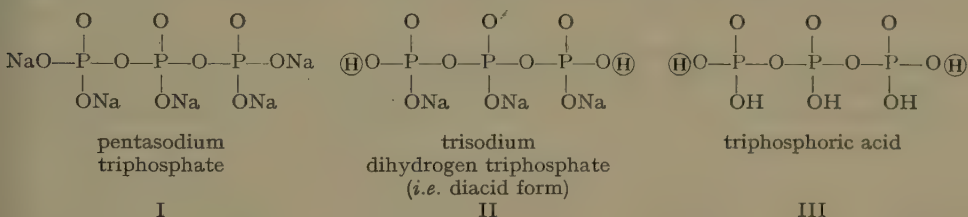It appears that up to about 0.03 g of sodium alkylarylsulphonate, i.e. about 0.02% at the end of the titration, can be tolerated, whether or not ammonium nitrate is used.

The difference between the series with and without ammonium nitrate is very striking. It seems likely that without ammonium nitrate there is a limit to the proportion of silver phosphate which will be precipitated in the presence of surface active

matter, and that this limit is reached at a pH somewhere between 4.8 and 6.0. Beyond this point further additions of alkali cause precipitation of silver hydroxide. Thus the rate of increase of pH with addition of alkali is very slow and the final result is too high. Both the slow change of pH and darkening due to the formation of silver hydroxide were observed during the experiments. In the experiments with ammonium nitrate this limit would not be reached. Consequently at pH 4.8 the liberated acid has been completely titrated, but the phosphate is incompletely precipitated (less completely in fact than in the other series) and the titration is therefore too low. The precise mechanism of this phenomenon is not understood, but it is reasonable to expect surface active substances to interfere in some way with the mechanism of flocculation of the initially colloidal silver phosphate.

DETERMINATION OF MEAN CHAIN LENGTH OF CONDENSED PHOSPHATES

"Chain length" is used here to mean number of phosphorus atoms per molecule. Straight-chain condensed phosphates have the general formula $Na_{n+2}P_nO_{3n+1}$, arranged in structures analogous to those shown below for triphosphate[15].

$$
\begin{array}{ccc}
\text{O} & \text{O} & \text{O} \\
\| & \| & \| \\
NaO-P-O-P-O-P-ONa \\
| & | & | \\
\text{ONa} & \text{ONa} & \text{ONa}
\end{array}
\qquad
\begin{array}{ccc}
\text{O} & \text{O}' & \text{O} \\
\| & \| & \| \\
\text{(H)}O-P-O-P-O-P-O\text{(H)} \\
| & | & | \\
\text{ONa} & \text{ONa} & \text{ONa}
\end{array}
\qquad
\begin{array}{ccc}
\text{O} & \text{O} & \text{O} \\
\| & \| & \| \\
\text{(H)}O-P-O-P-O-P-O\text{(H)} \\
| & | & | \\
\text{OH} & \text{OH} & \text{OH}
\end{array}
$$

pentasodium	trisodium	triphosphoric acid
triphosphate	dihydrogen triphosphate	
	(*i.e.* diacid form)	
I	II	III

The ringed hydrogen atoms in II and III are weakly acidic and may be titrated between pH values of 3.8 and 9.7 (for triphosphate; the corresponding values for other condensed phosphates decrease with increasing chain length). The remaining hydrogen ions in III are strongly acidic and are neutralised at pH 3.8. All straight-chain condensed acids have one strongly acidic hydrogen ion per phosphorus atom and one weakly acidic hydrogen atom at each end of the molecule.

VAN WAZER AND HOLST[16] determined the chain length of these substances by passing them through acid cation exchange resins to produce the free condensed acids, and plotting complete titration curves for these. All the curves showed two "steps", one at pH 3.5–4.0 and the other at pH 9–10. If V_1 ml is the volume required for the strongly acid hydrogen (*i.e.* the titration to the first "step") and V_2 ml the volume required by the weakly acid hydrogen (*i.e.* the titration between the two "steps") then $V_1/V_2 = n/2$ where n is the number of phosphorus atoms per molecule.

QUIMBY[17] determined the weakly acid hydrogen in the same way but calculated the number of strongly acid hydrogen ions from the total P_2O_5.

The method previously described for total P_2O_5 can also be used to determine the chain length of condensed phosphates. Such salts are converted to the diacid form $Na_nH_2P_nO_{3n+1}$ (analogous to II) by adjusting the pH to the value corresponding to the point of inflexion at the lower step of the titration curve. If the diacid form is treated with silver nitrate it reacts thus:

$$Na_nH_2P_nO_{3n+1} + (n+2)\, AgNO_3 \rightarrow Ag_{n+2}P_nO_{3n+1}\downarrow + n\, NaNO_3 + 2\, HNO_3$$
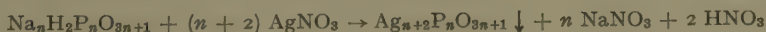
Each molecule thus yields two equivalents of hydrogen ion. If the phosphate is hydrolysed to the ortho-acid and analysed similarly, each molecule will yield n molecules of ortho-acid and therefore $2n$ hydrogen ions.

If these two experiments are performed on equal aliquots of the same solution, the mean chain length $\bar{n}$ is given by the ratio of the two titrations.

Procedure

Take a sample of condensed phosphate containing about 1 g of P_2O_5. It is satisfactory to assume the formula $(NaPO_3)_n$ in calculating the sample weight. Dissolve the sample in water, transfer it to a 250-ml volumetric flask and dilute to volume.

Place a 25-ml portion in a boiling flask, add 25 ml of 3 N nitric acid and boil gently under a reflux condenser for at least 30 min. Cool, transfer to a beaker and adjust the pH to 4.5. Add 10 ml of 10% silver nitrate solution and titrate to pH 6.0 with 0.1 N sodium hydroxide. Let this volume be V_2 ml.

While the first aliquot is boiling place a second 25-ml portion in a 250-ml beaker. Add 3 N nitric acid dropwise until the pH is about 3. Titrate slowly with 0.1 N sodium hydroxide, plotting pH against volume of alkali. Stop titrating as soon as a complete "step" has been plotted. From the graph determine the pH at which the slope is greatest. This is the pH at which the phosphate is present in its diacid form.

Readjust the pH to the value just determined, add 10 ml of 10% silver nitrate solution and titrate to pH 6.0 with 0.1 N sodium hydroxide. Let this volume be V_1 ml.

Mean chain length $\bar{n} = V_2/V_1$.

Results

This procedure was tested on pure samples of tetrasodium pyrophosphate, pentasodium triphosphate and hexaguanidinium tetraphosphate. The values found for the number of phosphorus atoms per molecule were 2.00, 3.02 and 4.00 respectively.

The diacid form of orthophosphate has a pH of 4.5. That of pyrophosphate is 4.2, and of triphosphate 3.8. For $n > 3$ the pH of the diacid form approaches a limiting value of about 3.5. Consequently mixtures of phosphates give less well-defined points of inflexion in their titration curves than single chemical entities, and even at the steepest point there will be some molecules present with too many hydrogen atoms and some with too few. (This is why the method of GERBER AND MILES[8] for orthophosphate in condensed phosphate is not entirely satisfactory; it is impossible simultaneously to have orthophosphate present exclusively as Na_2HPO_4 and pyro- and triphosphate present exclusively as $Na_4P_2O_7$ and $Na_5P_3O_{10}$ respectively). The resultant errors will, however, tend to cancel each other, as was shown by a test on a phosphate mixture recovered from a detergent powder. The method described gave a value for $\bar{n}$ of 2.66. The phosphate was analysed by ion exchange chromatography and a value for $\bar{n}$ calculated from the determined composition. It was 2.67.

This method of analysis may be regarded as a useful complement to the determination of total P_2O_5 on the one hand and the various chromatographic methods for determining the component phosphates on the other.

Great Britain for supplying samples of pure condensed phosphates, and Colgate Palmolive Limited for permission to publish this paper.

SUMMARY

A method has been developed for the volumetric determination of orthophosphate, and a simple variation permits the determination of the average number of phosphorus atoms per molecule in condensed phosphates. For total P_2O_5 the phosphates are converted to the diacid ortho-salt and precipitated as silver phosphate. The liberated acid is then titrated. For determination of chain length the condensed phosphate is converted to the diacid form and treated similarly, then hydrolysed and determined as orthophosphate. The ratio of the two titrations is equal to the average number of phosphorus atoms per molecule.

RÉSUMÉ

Une méthode a été mise au point pour le dosage volumétrique des phosphates. Le phosphate (sous forme de MH_2PO_4) est précipité par le nitrate d'argent; l'acide libéré est titré par l'hydroxyde de sodium. Un procédé est également décrit pour l'analyse des polyphosphates.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur volumétrischen Bestimmung von Phosphaten. Das Phosphat (als MeH_2PO_4) wird mit Silbernitrat gefällt und die dabei entstehende Säure titriert. In modifizierter Form kann die Methode auch zur Bestimmung der Kettenlänge kondensierter Phosphate verwendet werden.

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CATALYSTS FOR CERIUM(IV) OXIDIMETRY

DETERMINATION OF PHOSPHITE, HYPOPHOSPHITE, TELLURIUM AND MERCURY

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In a previous paper[1] a new catalyst system was developed, which would extend the scope of cerium(IV) oxidimetry by providing a simple, rapid method for the determination of many difficultly oxidizable inorganic and organic compounds. This method, which involves the use of silver(I) and manganese(II) salts as catalysts in conjunction with a perchloric acid solution of cerium(IV) sulfate, has been applied to the determination of mercury(I)[1], and to the evaluation of hydroxyorganic compounds as glycerol, erythritol, and 8-quinolinol[2].

Volumetric methods for phosphite and/or hypophosphite are oxidation by bromate[3] iodine[4], hypobromite[5], and vanadate[6]. Procedures for tellurium include reduction to the metal and corresponding oxidation with iodine[7]; and periodate[8] and dichromate[9] oxidation of tellurium(IV).

Many of these methods require either strict control of experimental conditions or heating for prolonged periods to achieve satisfactory results.

Rao and Rao[10] have proposed a catalytic oxidation of phosphite and hypophosphite with cerium(IV) sulfate, using silver sulfate, and Willard and Young[11] used chromium(III) sulfate to catalyze the ceric oxidation of tellurous acid. However time of reaction was still approximately 30 min in each instance.

Preliminary observations have shown that this new catalyst system greatly increases the rate of these reactions, thus providing a rapid method for the determination of these substances. Also a direct titration of mercury(I) is proposed using ceric perchlorate reagent, thus eliminating the necessity of back titration.

EXPERIMENTAL

All solutions were prepared from reagent grade chemicals and distilled water.

Cerium(IV) reagent, iron(II) solution, and mercury(I) perchlorate solution

All solutions 0.025 F, were described in a previous paper[1].

Ceric perchlorate solution

55 g of $(NH_4)_2Ce(NO_3)_6$ (G. F. Smith Chemical Co.) were added to 340 ml of 72% perchloric acid with stirring. The resulting solution was diluted to 1 l with water

and transferred to a dark reagent bottle, covered with black insulating tape. This reagent was standardized every two weeks against arsenious acid.

Catalyst solution (A)

2.8 ml of 50% manganese(II) nitrate solution (J. T. Baker Chemical Co.) and 3.0 g of silver(I) nitrate were dissolved in 250 ml of 1 F perchloric acid.

Catalyst solution (B)

1.2 ml of 50% manganese(II) nitrate solution and 5.0 g of silver(I) nitrate were dissolved in 100 ml of 1 F perchloric acid.

Phosphite and hypophosphite solutions

These solutions were prepared by dissolving 1.909 and 0.530 g of the reagent grade sodium salts (Fischer Scientific Co.) in 1 l of distilled water, respectively, and were standardized according to the method of RAO AND RAO[10].

Tellurium solution

1.0 g of tellurium oxide was dissolved (Fischer Scientific Co.) in 20 ml of conc. HCl. The resulting solution was boiled down with 55 ml of 16 M sulfuric acid, diluted to 1 l, and standardized by the procedure of WILLARD AND YOUNG[11].

RECOMMENDED PROCEDURES

Determination of phosphite and hypophosphite

To a solution containing 10–100 mg of phosphite or 5–35 mg of hypophosphite, add 2 ml of catalyst solution (B), 5.5 ml of conc. sulfuric acid per each 100 ml of solution, and a 70–150% excess of cerium(IV). Heat on a hot plate, preset on high (or 100°) for 7 min in the case of hypophosphite and 10 min for phosphite. Quench the reaction by cooling and addition of 10 ml of conc. sulfuric acid, and titrate with standard iron(II) solution, using ferroin indicator.

Determination of tellurium(IV)

Heat a mixture containing 5–60 mg of tellurium, 1 ml of catalyst solution (A), 17 ml of 72% perchloric acid per each 100 ml of solution, and a 50–150% excess of cerium(IV) reagent on a hot plate at 95° until the solution rapidly turns cherry red in color. Quickly quench the reaction and proceed as described in the determination of phosphite.

The solution may be brown at the start of oxidation, but will gradually turn light yellow, and then red at the end-point. The reaction time is 3–7 min for 5–60 mg samples of tellurium. For best results the solution should not be boiled, nor heated past the formation of the cherry red color of permanganate. Because a small, nearly constant amount of oxidant is lost in the production of the red color, a blank correction should be applied (about 0.005 mequiv.). This may be determined by following the recommended procedure, but omitting the tellurium. The red color will appear upon heating. The difference between the mequiv. of iron(II) solution required for back titration and the number of mequiv. of cerium(IV) actually present represents the blank correction.

Determination of mercury(I)

Heat a solution containing 50–400 mg of mercury(I), 17 ml of 72% perchloric acid per each 100 ml of solution, and 1 ml of catalyst solution (A) to boiling. Immediately titrate with the ceric perchlorate solution, stirring continuously, to almost the end-point (which is the first permanent yellow color). Cool to 50–60°, add 2 drops of nitroferroin indicator, and continue the titration until the red color of the indicator disappears. If the end-point has already been passed, back titrate with standard iron(II) solution to the first tinge of pink.

DISCUSSION

Phosphite and hypophosphite

Due to the formation of insoluble cerium phosphite and phosphate in perchloric acid solutions, it proved impossible to use this acid media. Although reaction is much slower and the red end-point is not obtained in sulfuric acid solution, precipitation does not occur, and reaction proceeds smoothly. A 1.0-F sulfuric acid concentration proved optimum in both cases.

The amount of catalyst in solution (B) proved to be optimum for both determinations, reaction proving too slow and sluggish with catalyst (A). For best results in each determination, the per cent excess cerium(IV) reagent should be above 50% (Table I). Below this, incomplete oxidation occurs, causing low results.

TABLE I

EFFECT OF PER CENT EXCESS CERIUM(IV) REAGENT

Excess cerium(IV) %	Na_2HPO_3, mg		NaH_2PO_2, mg		Tellurium, mg	
	Present	Found	Present	Found	Present	Found
30.0	—	—	—	—	53.00	53.40
50.0	85.91	85.10	26.50	26.35	53.00	53.19
75.0	85.91	85.84	26.50	26.45	53.00	52.87
100.0	85.91	85.89	26.50	26.60	53.00	52.84
150.0	85.91	86.07	26.50	26.60	53.00	52.99

Heating periods of 7 and 10 min were found to be sufficient for all samples of hypophosphite and phosphite analyzed. However, the solution could be heated for one hour without error (Table II).

TABLE II

EFFECT OF OVERHEATING ON PHOSPHITE DETERMINATION

Time of reaction min	Na_2HPO_3, mg	
	Present	Found
10.0	85.95	85.99
15.0	85.95	85.99
30.0	85.95	85.99
60.0	85.95	85.99

The amount of each material may be calculated as follows:

$$\text{mg } Na_2HPO_3 = \frac{\text{mol. wt.}}{2} \text{ [net mequiv. of cerium(IV)]}$$

$$mg\ NaH_2PO_2 = \frac{mol.\ wt.}{4}\ [net\ mequiv.\ of\ cerium(IV)]$$

Tellurium

Indication of the point of complete oxidation of tellurium(IV) depends upon the amount of excess cerium(IV) present. When 50% or more excess cerium is available, oxidation of the manganese catalyst to the cherry red of permanganate occurs at the point of complete oxidation. However the turbidity of manganese(IV) oxide does not occur at the equivalence point when the cerium(IV) reagent is below 50% excess as in the mercury(I) determination described previously[1], and the percent excess cerium(IV) should be above 50% for best results (Table I).

A 2.0-F perchloric acid concentration was found to be optimum. In 1.0-F acid the cherry red color does not readily appear, whereas in concentrations above 2.0-F there is additional error due to decomposition of excess cerium(IV) reagent by the catalysts.

RESULTS

Results of the determinations of phosphite, hypophosphite, tellurium(IV), and mercury(I) are shown in Table III. Samples of Na_2HPO_3 and NaH_2PO_2 ranging from 15–100 mg and 5–32 mg were evaluated with standard deviations of ±0.17 and

TABLE III

DETERMINATION OF PHOSPHITE, HYPOPHOSPHITE, TELLURIUM AND MERCURY

Na₂HPO₃, mg		NaH₂PO₂, mg		Error, %	
Present	Found	Present	Found	Phosphite	Hypophosphite
15.27	15.30	5.300	5.318	+0.19	+0.34
19.09	19.15	10.60	10.63	+0.31	+0.28
38.18	38.25	15.90	15.86	+0.18	—0.25
57.27	57.37	21.20	21.13	+0.17	—0.33
85.91	85.99	26.50	26.60	+0.093	+0.38
85.91	85.89	29.50	29.63	—0.023	+0.47
95.45	95.35	31.80	31.70	—0.10	—0.31
				$\sigma = \pm0.17$	$\sigma = \pm0.32$

Tellurium, mg		Mercury, mg		Error, %	
Present	Found	Present	Found	Tellurium	Mercury
10.40	10.42	67.80	68.20	+0.19	+0.49
21.20	21.24	90.00	89.90	+0.18	—0.11
39.75	39.84	113.0	113.8	+0.25	+0.70
53.00	52.99	158.2	158.3	—0.019	+0.068
69.62	69.80	253.6	252.0	+0.24	—0.60
84.10	84.34	355.0	354.3	+0.28	—0.18
106.0	105.7	507.0	505.0	—0.30	—0.38
				$\sigma = \pm0.21$	$\sigma = \pm0.36$

±0.32% respectively. 10–106 mg samples of tellurium(IV) were determined, using the red color of permanganate as end-point indication, with a standard deviation of ±0.21%.

Finally, 65–500-mg samples of mercury(I) were analyzed with a deviation of

$\pm 0.36\%$. These results may be compared to the indirect determination of mercury(I) in a previous paper, in which standard deviations of ± 0.22 and $\pm 0.32\%$ were obtained using the red permanganate color and the formation of manganese(IV) oxide as end-point indications[1]. The advantage of direct titration with ceric perchlorate solution is compensated by the disadvantage that ceric perchlorate is unstable, and must be restandardized every two weeks. The results by each method are comparable.

A photometric titration of mercury(I) with ceric perchlorate was attempted at 410 mμ, using the same conditions as described above. Samples ranging from 65–160 mg of mercury(I) were analyzed with a deviation of about $\pm 0.5\%$. Results were, in general, not as good as in the described procedure.

The presence of possible interferences in all determinations was studied briefly. All organic and inorganic substances oxidized by ceric under these conditions will interfere.

There is no differentiation of phosphite and hypophosphite possible under these catalytic conditions. If mixtures are to be determined, hypophosphite alone may be analyzed using the method of BERNHARDT[12], and then both substances determined catalytically.

SUMMARY

A new catalytic oxidation procedure, involving the use of a cerium(IV) sulfate reagent in perchloric acid with a mixed silver(I)–manganese(II) perchlorate catalyst, has been developed for the determination of phosphite, hypophosphite, and tellurium. By this method 15–100 mg of phosphite, 5–35 mg of hypophosphite, and 10–105 mg of tellurium may be determined with standard deviations of ± 0.17, ± 0.32, and $\pm 0.21\%$ respectively. A direct titration procedure for mercury(I) is described using a ceric perchlorate solution as titrant with the mixed catalyst system. Samples from 65–510 mg may be analyzed with a standard deviation of $\pm 0.36\%$.

RÉSUMÉ

Un nouveau procédé est proposé pour le dosage des phosphites, des hypophosphites et du tellure, au moyen de sulfate de cérium(IV), en solution perchlorique. On utilise comme catalyseur un mélange de perchlorate d'argent(I) et de manganèse(II). Un titrage est également décrit pour le dosage du mercure(I).

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Phosphit, Hypophosphit und Tellur mit Hilfe von Cer(IV)-sulfat in perchlorsaurer Lösung in Gegenwart eines Katalysators (Mischung von Silber- und Mangan(II)-perchlorat). Nach dieser Methode kann auch Quecksilber(I) bestimmt werden.

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A COMPLEXOMETRIC TITRATION OF INORGANIC SULPHATE IN SYNTHETIC DETERGENTS

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A well-known method for the determination of sodium sulphate in synthetic detergents is to extract organic compounds with the aid of alcohol[1] or of 1 : 1 acetone–ethyl ether[2] and to determine the sodium sulphate as barium sulphate. When, however, the anionic detergent is a triethanolamine salt instead of a sodium salt this method fails, because triethanolamine sulphate is soluble in alcohol and the residue of the extraction with 1 : 1 acetone–ethyl ether is not crystalline. Moreover, the sodium salts of some alkyl ether sulphates do not readily dissolve in 1 : 1 acetone–ethyl ether, so that a quantitative separation from organic material, if at all possible, is very difficult to effect.

The purpose of this work was to overcome the above-mentioned difficulties and to find a rapid titrimetric method which avoids the time-consuming separation of sodium sulphate from the anionic active ingredient by solvent extraction. We found that the indirect titration of inorganic sulphate according to ANDEREGG et al.[3] cannot be used to determine sulphate in synthetic detergents owing to the interference of anionic surface-active agents, although the results are very good when no anionic synthetic detergents are present. A sharp end-point is reached also if the anionic synthetic detergent solution contains no sulphate and all the added barium is bound quantitatively by EDTA (See Table I). However, the values obtained by this titrimetric method for the recovery of added sulphate from sulphate-free anionic detergents were too low.

At first we supposed that the barium sulphate was not quantitatively precipitated, because insufficient barium chloride was present to precipitate both sulphate and lauryl sulphate as their barium salts. However, addition of an excess of barium chloride still gave low results. Sometimes the colour change was very sluggish.

SIJDERIUS[4] also obtained low results when the excess barium chloride was titrated immediately after boiling for some seconds and cooling. We therefore titrated sulphate in the presence of an anionic surface-active agent 24 h after boiling and cooling, but again obtained low results. If, after precipitation of sulphate as barium sulphate, lauryl sulphate was added, variable values were found depending on the time elapsed after precipitation. When lauryl sulphate was added immediately after precipitation low values were always obtained. Therefore we suppose that the barium sulphate is solubilised by the anionic detergent. The cationic surface-active agent cetyl pyridinium chloride (C.P.C.) does not interfere in the titration of sulphate, hence we tried

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to bind the anionic surface-active agent as a salt with this cationic agent and thus we
succeeded in eliminating the solubilising action.

As the solution of C.P.C. and Eriochrome Black T has itself a blue colour, the latter
compound cannot be used as indicator in this method. We did not check whether
sulphate can be titrated in this manner in the presence of other cationic surface-active
agents.

<div align="center">METHOD</div>

Reagents

EDTA solution, 0.01 M: Dissolve 3.721 g disodium ethylenediaminetetraacetate
dihydrate in 1 l of distilled water. Barium chloride solution, approximately 0.01 M:
Dissolve 2.443 g barium chloride (A.R. grade), $BaCl_2 \cdot 2 H_2O$, in distilled water and
dilute to 1 l (Note I). Cetyl pyridinium chloride, $C_{16}H_{33} \cdot C_5H_5N \cdot Cl \cdot H_2O$. (Pharma-.
ceutical grade from Leda Chemicals Ltd., London). Indicator: Dissolve 0.09 g Metal-
phthalein (Phthalein Purpur obtained from Riedel-de Haën A.G., Seelze-Hannover)
and 0.005 g Naphthol Green B in 0.5–1 ml aqueous ammonia (25%) and dilute with
distilled water to 50 ml. This aqueous indicator solution is stable for one week (Note 2).

Procedure

Weigh a sample which contains approximately 0.02 g of sulphate, transfer to a
250-ml glass beaker and dissolve in 40 ml of distilled water. Add a small excess of
C.P.C. (The requisite amount of C.P.C. can be determined by cationic titration of the
anionic detergent according to EPTON[5] and WIJGA[6]). Acidify with 2 ml of 0.5 N hydro-
chloric acid and add 25 ml of the 0.01 M barium chloride solution. Heat and boil
gently for 1–2 min. After cooling add 2 ml of indicator solution and 7.5 ml of aqueous
25% ammonia (Note 3). Titrate rapidly — to prevent formation of barium carbonate—
with the 0.01 M EDTA solution. After the end-point has been reached add a small
excess of the EDTA solution (Note 4). Add 100 ml of 96% ethanol and titrate with
the barium chloride solution to a colour change from pale green to pale violet (Note 5).

Calculation

$$\frac{[(25 + a)t - 0.01\, b] \cdot 96 \cdot 100}{c} = d$$

a = ml of approximately 0.01 M barium chloride solution required for back-titra-
   tion
t = molarity of barium chloride solution
b = ml of 0.01 M EDTA solution required for titration
c = mg of sample
d = percentage of sulphate ions in the sample.

Notes

1. The barium chloride solution must be standardized by the following procedure
Weigh approximately 550 mg of A.R. grade sodium sulphate, transfer to a 250-ml
volumetric flask and dilute with water to 250 ml. Pipette 10 ml of the solution and
titrate according to the described procedure without adding C.P.C.
2. If the end-point is not sharp, the indicator solution must be renewed.
3. The best results are obtained at a pH of approximately 11.

4. Sometimes only a change in colour intensity takes place, or the change is not perceptible at all. If after the addition of alcohol the colour is violet, some more EDTA solution must be added.

5. The end-point is satisfactory and is always obtained correctly by experienced analysts. If the solution of the synthetic detergent is coloured, Naphthol Green B must be omitted from the indicator solution.

RESULTS AND DISCUSSION

Table I lists the titrations of barium with EDTA in anionic synthetic detergent solutions which contain no inorganic sulphate; no C.P.C. was added.

TABLE I

THE RECOVERY OF BARIUM FROM SULPHATE-FREE ANIONIC SYNTHETIC DETERGENTS

Anionic	mg anionic	ml BaCl₂ 0.01 M added	ml EDTA 0.01 M found
Sodium alkyl aryl sulphonate	247.4	25.84	25.88
	521.3	25.81	25.87
Dioctyl ester of sodium sulphosuccinic acid	266.0	25.66	25.74
	490.5	25.29	25.38
Sodium lauryl sulphate	248.8	26.23	26.26
	504.9	26.09	26.10
Oleic acid ester of sodium isethionate	291.8	26.40	26.46
	524.8	25.93	25.98
Sodium alkyl naphthalene sulphonate	237.9	25.66	25.74
	501.4	25.69	25.59
Sodium palmitate	263.0	25.88	25.07
	526.3	27.49	26.37

The difference between added and recovered barium is less than 0.1 ml of 0.01 M barium chloride solution except in the case of sodium palmitate when greater differences are caused by the insolubility of palmitic acid, which occludes barium palmitate.

From the determinations of sodium sulphate in a solution of sodium lauryl sulphate without the addition of C.P.C. the following results are mentioned: From a solution containing 20.02 mg of sodium sulphate and 100 mg of sodium lauryl sulphate in different experiments only 15.76, 14.45, 13.60, 15.43 and 14.40 mg of sodium sulphate were recovered if the quantity of barium chloride added (0.25 mmole) was insufficient to precipitate both sulphate and lauryl sulphate. With an excess of barium chloride (0.25 mmole), 19.84, 19.75, 19.04, 19.18 and 19.24 mg of sodium sulphate were found by titration of solutions containing 20.01 mg of sodium sulphate and 50 mg of sodium lauryl sulphate.

The results of the sulphate determinations in sodium lauryl ether sulphate solutions by the described method are presented in Table II.

The 95% confidence intervals are calculated from these data and are —ɔ.11 to 0.00 and 25.03 to 25.13, respectively.

The results of a number of determinations performed according to the procedure described are shown in Table III.

TABLE II

THE DETERMINATION OF SULPHATE IN SODIUM LAURYL ETHER SULPHATE

Anionic + C.P.C.			Anionic + C.P.C. + Na₂SO₄		
Anionic mg	C.P.C. mg	Na₂SO₄ found, mg Y	Anionic mg	C.P.C mg	Na₂SO₄ found, mg Y
324.8	353.0	—0.06	257.3	258.8	25.03
582.6	613.6	—0.16	588.0	648.3	25.03
427.2	441.5	—0.10	355.0	363.8	25.21
803.0	805.9	—0.04	426.5	434.1	25.05
569.4	584.8	+0.03	573.5	640.1	25.05
332.1	350.6	+0.03	399.8	419.7	25.13
429.9	438.7	—0.03	349.6	397.1	25.11
226.6	245.9	—0.09	191.6	203.8	25.02
		$\bar{Y} = $ —0.05			$\bar{Y} = $ 25.08
Standard deviation		$S = $ 0.07	Standard deviation		$S = $ 0.07
Added Na₂SO₄, mg		nil	Added Na₂SO₄, mg		= 25.03

TABLE III

DETERMINATION OF SULPHATE IN VARIOUS ANIONIC SURFACE-ACTIVE AGENTS

Anionics	n[a]	Na₂SO₄ added mg	Na₂SO₄, found mg, $\bar{Y}$	S[b]	95% Confidence interval
Sodium alkyl aryl sulphonate	7	nil	0.00	0.03	—0.03– 0.03
	7	22.99	23.13	0.04	23.09– 23.17
Dioctyl ester of sodium sulphosuccinic acid	8	nil	0.20%[c]	0.02	0.18– 0.22%[c]
	7	10.49	10.50[d]	0.09	10.43– 10.58[d]
	7	23.13	23.15[d]	0.10	23.05– 23.24[d]
Sodium lauryl sulphate	9	nil	0.05	0.05	0.01– 0.09[e]
	7	22.99	23.01	0.06	22.96– 23.07[e]
Sodium lauryl ether sulphate (see Table II)	8	nil	—0.05	0.07	—0.11– 0.00
	8	25.03	25.08	0.07	25.03– 25.13
Oleic acid ester of sodium isethionate	7	nil	—0.11	0.06	—0.16––0.05[f]
	8	24.99	24.89	0.06	24.84– 24.94
Sodium alkyl naphthalene sulphonate	8	nil	0.01	0.03	—0.02– 0.03
	8	24.87	24.95	0.06	24.90– 25.00
Sodium palmitate	4	nil	0.00	0.05	—0.07– 0.07
	4	24.99	25.01	0.04	24.95– 25.07

[a] Number of experiments
[b] Standard deviation
[c] % Na₂SO₄ in dioctyl ester of sodium sulphosuccinic acid
[d] Corrected for blank
[e] A heavy precipitate is formed after the addition of alcohol
[f] Indicator: Metalphthalein, colour change from yellow to orange; the solution of this anionic has a yellow colour.

In the experiments summarised in Table III 20c–800 mg of anionic and correspond-ing amounts of C.P.C. were used. The anionics were freed from inorganic sulphate by

repeated extraction with absolute ethanol, etc. Only the dioctyl ester of sodium sulphosuccinic acid was not completely free from sulphate. The titrations without the addition of sodium sulphate and the use of different amounts of this anionic (300–670 mg) resulted in a percentage of 0.20% sodium sulphate. The masking effect of this anionic — inorganic sulphate is not quantitatively precipitated as barium sulphate — is demonstrated by the fact that the recovery of barium in the same sample without the addition of C.P.C. is nearly quantitative (See Table I).

The results indicate very good accuracy and reproducibility. An inorganic sulphate determination in duplicate by the described method is done within an hour.

SUMMARY

An accurate method for the determination of inorganic sulphate in synthetic detergents has been developed. After addition of a cationic surface-active agent (cetyl pyridinium chloride) to an anionic detergent, sulphate can be determined by means of indirect titration with EDTA, using a mixture of Metalphthalein and Naphthol Green B as indicator.

RÉSUMÉ

Une méthode a été mise au point pour le dosage de sulfate dans des détergents synthétiques. On effectue un titrage indirect au moyen de l'acide éthylènediaminotétracétique, après addition de chlorure de baryum.

ZUSAMMENFASSUNG

Beschreibung einer Methode zur Bestimmung von Sulfat in synthetischen Waschmitteln durch indirekte Titration mit Aethylendiaminotetraessigsäure nach Zugabe von Bariumchlorid.

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THERMOGRAVIMETRIC DETERMINATION OF MAGNESIUM, POTASSIUM AND LEAD BY PRECIPITATION WITH DILITURIC ACID

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INTRODUCTION

Dilituric acid (5-nitrobarbituric acid) was first prepared in 1845 by SCHLIEPER[1] and many of its salts shortly thereafter[1,2]. Despite the fact that this was about a hundred years ago, relatively little is known about them even today. The solubilities of a number of diliturate salts have been measured by REDEMANN AND NIEMANN[3]. Dilituric acid has been proposed for use as a precipitating agent for the determination of a number of cations and also for several organic bases[3-5]. DICK used dilituric acid for the determination of copper, cadmium, cobalt, and nickel[5] and DE GRAAFF AND NOYONS[6] reported a method for potassium. These methods offer the advantage of rapidity, accuracy and favorable gravimetric factor but suffer from the lack of specificity.

Methods for the determination of magnesium and potassium have been developed by us and the determination of lead has also been investigated. Thermolysis curves have been established for these precipitates to ascertain their compositions and thermal stabilities. The thermolysis curve for $MgNH_4PO_4 \cdot 6H_2O$ has also been traced since the magnesium solution used in these determinations was standardized by precipitation as $MgNH_4PO_4 \cdot 6H_2O$ and it was thought desirable to investigate the thermal conditions for the conversion of $MgNH_4PO_4 \cdot 6H_2O$ to $Mg_2P_2O_7$.

THERMOLYSIS CURVES

Many complexes and salts which have been proposed for the gravimetric determination of metallic cations suffer from a lack of thermal stability, rendering their use problematic in many cases. For example, $Mg(NH_4)_2Fe(CN)_6$ proposed by FEIGL AND PAVELKA[7] for the determination of magnesium is unstable above 50°. As a further example ZAN'KO AND BURSUK[8] recommend drying lead dibromo-5,7-oxinate at 195° to 215° in a proposed quantitative method but it has been shown by its thermolysis curve that it does not correspond to this composition[9].

The thermolysis curves for magnesium, potassium and lead diliturates have been obtained to investigate the quantitative utility of these compounds. The thermolysis curves for magnesium, potassium and lead diliturate show that their stabilities are quite adequate for their utilization in gravimetric determinations.

Experimental

Equipment

An ADAMEL recording thermobalance (Chevenard System) was used to obtain the thermolysis curves.

Salts of dilituric acid

Potassium diliturate. A hot solution of saturated dilituric acid at 25° was added in excess to a solution of reagent grade potassium chloride in water. Anhydrous potassium diliturate ($KC_4N_2H_2O_3 \cdot NO_2$) formed after a few minutes. The solution was cooled in an ice bath, and the precipitate was filtered, washed with water and dried at 100° for one hour.

Magnesium diliturate octahydrate. A 0.02-M solution of Merck reagent grade magnesium sulfate was treated with an excess of saturated dilituric acid solution. The magnesium diliturate octahydrate [$Mg(C_4N_2H_2O_3 \cdot NO_2)_2 \cdot 8H_2O$] precipitate was left to form for several hours, cooled, filtered, and washed twice with a 0.02% dilituric acid solution in 50% ethanol and finally with anhydrous ether.

Lead diliturate dihydrate. Saturated dilituric acid was added to reagent grade lead nitrate in water. The solution was allowed to stand overnight. A compact crystalline deposit of lead diliturate [$Pb(C_4N_2H_2O_3 \cdot NO_2)_2 \cdot 2H_2O$] formed. The crystals were filtered and washed with a water solution containing a small concentration of lead nitrate; they were then dried for one hour in an oven at 75°.

Carbon and hydrogen analyses of the above compounds are as follows:

	Calculated	Analysed
Potassium diliturate $KC_4N_2H_2O_3 \cdot NO_2$ mol. wt. 211.18	C: 22.75%; H: 0.96%	C: 23.27%; H: 1.15% C: 23.12%; H: 0.95%
Magnesium diliturate octahydrate $Mg(C_4N_2H_2O_3 \cdot NO_2)_2 \cdot 8H_2O$ mol. wt. 512.64	C: 18.74%; H: 3.94%	C: 19.24%; H: 3.93% C: 19.33%; H: 4.16%
Lead diliturate dihydrate $Pb(C_4N_2H_2O_3 \cdot NO_2)_2 \cdot 2H_2O$ mol. wt. 587.43	C: 16.36%; H: 1.38%	C: 16.76%; H: 1.32% C: 16.62%; H: 1.50%

Magnesium ammonium phosphate hexahydrate. This compound ($MgNH_4PO_4 \cdot 6H_2O$) was formed from a 0.0216-M solution of magnesium sulfate using the procedure of LUNDELL AND HOFFMAN[10].

Method

The thermolysis curves, Fig. 1, were obtained by heating the diliturates in No. 000 porcelain crucibles, while magnesium ammonium phosphate hexahydrate was heated in a No. 8, medium porosity, sintered glass filter. The weights of the samples and the corresponding rates of heating are given in Fig. 1. All the samples were heated in air with the exception of magnesium diliturate which was run in dry nitrogen flowing at the rate of 2 l per hour.

Discussion

The thermolysis curve of potassium diliturate has been determined previously by
DUVAL[9]. He mentions that very little decomposition is observed before 400° while a
mild explosion occurs towards 500°.

Fig. 1. Thermal decomposition curves
of metal diliturates and of magnesium
ammonium phosphate hexahydrate.
A. Potassium diliturate, 373.8 mg
heated at 300°/h; B. Magnesium dili-
turate octahydrate, 109.5 mg heated
at 65°/h; C. Lead diliturate dihydrate,
37.6 mg heated at 150°/h; D. Magne-
sium ammonium phosphate hexahy-
drate, 106.8 mg heated at 65°/h.

We have found that anhydrous potassium diliturate was stable to 250° on heating,
but decomposed rapidly between 250° and 355°. Above 355° there was a slow de-
composition terminating at 1040° with the production of K_2O. At 770° there was an
inflection point corresponding to the composition of K_2CO_3. Potassium diliturate
prepared by the same method but not dried previously in the oven gave the same
type of thermolysis curve.

The dehydration of magnesium diliturate octahydrate started at 100° and pro-
ceeded in two steps. An intermediate semistable hydrate was formed at 140°, after
the loss of four molecules of water; after the loss of four additional molecules of water
the anhydrous compound was obtained, stable between 220 and 260°. Above 260°
there was a rapid but nonexplosive decomposition. An inflection point found at 440°
corresponded to a weight 8% larger than would be the weight of $MgCO_3$. At 580°
constant weight was obtained which was 11% of the original weight and corresponded
to slightly more than the percentage weight of MgO. When an X-ray powder dif-
fraction pattern was taken of the residue it gave only lines corresponding to MgO.

Lead diliturate formed a compound stable to 180°. The decomposition which fol-
lowed to 260° produced a loss in weight corresponding to two molecules of water.
A subsequent fast decomposition occurred up to 370°; from there a slow decomposition
took place to 700° with an inflection point at 470°. The weight at 470° corresponded
to $PbCO_3$ and at 700° to PbO.

The thermal decomposition curve of magnesium ammonium phosphate hexa-
hydrate has been described by DUVAL[9]. He gave 46° as the temperature at which
dehydration begins and 477° as the temperature at which the total conversion to
$Mg_2P_2O_7$ is reached. The heating rate used by DUVAL was 300°/h. In our experimental
work with a heating rate of 65°/h the dehydration started at 40° and $Mg_2P_2O_7$ was
obtained at 350°. An inflection point occurred after a loss corresponding to the weight
of 6 H_2O or 5 molecules of water and one of ammonia. When a heating rate of 150°/h
was used dehydration began at 80° and the decomposition was terminated at 420°.
It is quite likely therefore that the higher temperature recommended by certain

authors for the pyrolysis of magnesium ammonium phosphate is necessary because of a fast rate of heating (above $1000°/h$). As an explanation, under such conditions an impermeable coating of fused $Mg_2P_2O_7$ probably forms on the precipitate particles rendering difficult the subsequent escape of the remaining water and ammonia.

THERMOGRAVIMETRIC DETERMINATION OF MAGNESIUM WITH DILITURIC ACID

There are numerous methods for the determination of magnesium. When magnesium is present in concentrations larger than $0.02\ M$ and with amounts larger than 10 mg, gravimetric, volumetric or complexometric methods are most suitable.

Among the best gravimetric methods for minimum amounts of magnesium is precipitation with tropeolin oo[11] or with 8-hydroxy-quinaldine[12]. The latter method permits a very good separation of magnesium from calcium and many other cations. When the amounts of magnesium are larger, the best gravimetric methods involve precipitation with 8-hydroxyquinoline[13] or with diammonium hydrogen phosphate[14]. The diammonium hydrogen phosphate method though frequently used is subject to a number of criticisms, namely slow precipitate formation, reprecipitation to improve purity of precipitate and time-consuming ignition to the pyrophosphate.

Since magnesium forms the most insoluble diliturate thus far reported in the literature[3] it seemed to offer possibilities as a rapid and accurate method for the determination of magnesium.

Experimental

Solutions

Standard magnesium solution. This solution was prepared from recrystallized reagent-grade anhydrous magnesium sulfate, dried for two hours at $100°$. The concentration was 0.524 mg of Mg/ml or $0.0216_4\ M$. The magnesium content of this solution was verified by analysis as the pyrophosphate (see discussion section) with a deviation of 2 p.p.m. from its concentration by weight. Since this is within the experimental error of the method the original standard value was used.

Dilituric acid solution. The dilituric acid solution was prepared by saturating a 50% ethanol solution with recrystallized dilituric acid trihydrate. Solution was accelerated by heating; the excess dilituric acid was filtered off after cooling. This solution was about $0.05\ M$.

Method of analysis

10-ml aliquots of the standard magnesium solution were treated with 25 ml of the dilituric acid solution. (Other volumes of magnesium were treated with proportionate volumes of reagent so that a molar ratio of D/Mg of about 5/1 was used). The magnesium diliturate was left to form for no more than 30 min at room temperature. It was then cooled in ice and filtered on a glass fritted filter of medium porosity. The precipitate was washed with saturated dilituric acid solution and finally with 95% ethanol. For the thermogravimetric determination the sintered glass filter containing the precipitate was placed on the thermobalance, preheated to a temperature between 70 and $90°$. Constant weight for the octahydrate was obtained in about 10 min. The heating cycle of the furnace was then started at $300°/h$ until a temperature of about $220°$ was reached, and the furnace then thermostated. The weight of the anhydrous precipitate was recorded. In this way two values for the amount of magnesium present were obtained.

Analytical results

Table I lists the results obtained by this method. The magnesium concentration in
the above determinations was 0.526 mg/ml with the exception of 0.105 mg/ml for the
1-mg sample and 0.263 mg/ml for the 5-mg samples.

TABLE I

THERMOGRAVIMETRIC DETERMINATION OF MAGNESIUM AS DILITURATE

Ppt. (mg)	Mg taken (mg)	Mg found (mg)	Dev. (mg)
Weighed as MgD$_2$·8H$_2$O			
22.4	1.05	1.06	+0.01
56.3	2.63	2.67	+0.04
56.6	2.63	2.68	+0.05
109.8	5.26	5.21	—0.05
109.6	5.26	5.20	—0.06
110.0	5.26	5.22	—0.04
109.9	5 26	5.21	—0.05
110.9	5.26	5.26	0.00
110.9	5.26	5.26	0.00
110.0	5.26	5.26	0.00
110.6	5.26	5.25	—0.01
546.4	26.32	25.92	—0.40
546.1	26.32	25.90	—0.42
Reweighed as MgD$_2$			
16.1	1.05	1.06	+0.01
41.4	2.63	2.73	+0.10
41.3	2.63	2.72	+0.09
79.4	5.26	5.24	—0.02
79.5	5.26	5.25	—0.01
79.4	5.26	5.24	—0.02
79.2	5.26	5.23	—0.03
80.4	5.26	5.31	+0.05
80.2	5.26	5.29	+0.03
79.7	5.26	5.26	0.00
79.9	5.26	5.27	+0.01
395.5	26.32	26.40	—0.22
394.1	26.32	26.01	—0.31

In Table II are listed the results showing the interference of calcium in the determi-
nation of magnesium as magnesium diliturate and in Table III are shown the effects
of large dilution of the magnesium solution, very rapid dehydration of the octa-
hydrate as well as the precipitation of magnesium diliturate in the presence of oxalate
ions upon the magnesium results.

Discussion of results

The results for the determination of magnesium obtained in Table I are slightly lower
than the primary standard values in the case of the larger amounts of magnesium
(about 0.02 mg or 0.4% on the average). Solubility calculations indicate that under

our experimental conditions the maximum solubility of magnesium should be only $8 \cdot 10^{-6}$ mg. This is a negligible percentage loss of the total magnesium present.

When the concentration of magnesium was small (0.033 mg/ml) appreciable negative deviations (see Table III) were obtained. A solubility calculation similar to the one above indicates that the amount of magnesium left in solution should not exceed $7 \cdot 10^{-4}$ mg. This amount is too small to account for the increase in experimental error.

The standardization of the magnesium solution with pyrolysis of the magnesium ammonium phosphate in an electric muffle furnace at 1100° according to the

TABLE II

CALCIUM INTERFERENCE IN THE PRECIPITATION OF MAGNESIUM DILITURATE

Ca present (mg)	Conc. Ca (mg/ml)	Excess Ppt. (mg)	Ca Pptd. (mg)	Time for Ppt. formation
0.16	0.004	1.20	0.11	22 h
0.80	0.018	6.80	0.49	25 min
0.80	0.018	7.41	0.53	12 h

TABLE III

EFFECT OF CONCENTRATION, RATE OF HEATING AND OXALATE INTERFERENCE ON THE DETERMINATION OF MAGNESIUM AS MAGNESIUM DILITURATE OCTAHYDRATE

| Conc. Mg taken (mg/ml) | Weighed as $MgD_2 \cdot 8H_2O$ | | | Reweighed as MgD_2 | |
	Mg taken (mg)	Mg found (mg)	Dev. (mg)	Mg found (mg)	Dev. (mg)
0.263[a]	2.63	2.68	+0.05	2.72	+0.09
0.263[b]	2.63	2.67	+0.04	2.73	+0.10
0.033	5.26	5.05	—0.21	5.53	+0.27
0.088	5.26	5.19	—0.07	5.40	+0.14
0.263	5.26	5.20	—0.06	5.65	+0.39

The precipitates from the 5.26-mg samples of magnesium were dehydrated at a rate of heating above 700°/h.
[a] does not contain oxalate
[b] is 0.0269 M in respect to oxalate

LUNDELL AND HOFFMAN method gave an average of 0.518_7 mg/ml of Mg. It is possible, as mentioned by them, that some decomposition of the precipitate occurred at that temperature.

With the modified procedure the precipitation was identical. The precipitate was filtered through a fritted glass filter. It was first dried at 70° in the thermobalance to obtain $MgNH_4PO_4 \cdot 6H_2O$ and then decomposed to $Mg_2P_2O_7$ by heating to 620° at the rate of 150°/h.

An average magnesium concentration of 0.525_7 mg/ml was obtained from the hydrate and 0.529_3 mg/ml from the $Mg_2P_2O_7$. This gives an overall average of 0.527_5 mg/ml or a deviation of $+2\%$ from the value taken as standard.

In order to dehydrate magnesium diliturate octahydrate heating at a temperature of 220° is necessary. At 300°/h, the rate of heating normally used, it takes 45 min to

reach this temperature. Heating at 700°/h would shorten the heating time to less than 20 min but gave magnesium results about 6% above the weight of magnesium taken (see Table III). This probably is due to incomplete dehydration as in the pyrolysis of magnesium ammonium phosphate hexahydrate.

The determination of magnesium by precipitation with dilituric acid is not possible in the presence of calcium, since calcium interferes even at very low concentrations. A solubility calculation for our experimental conditions shows that the solubility product of calcium diliturate is exceeded only when the concentration of calcium is in excess of 0.08 mg/ml. The highest concentration of calcium that we have used is 0.018 mg/ml (see Table III), which is well below the maximum allowable concentration according to the solubility calculation, but coprecipitation nevertheless takes place. In the two samples containing 0.80 mg of calcium the precipitates were left to form for 25 min in one case and for 12 h in the other. The amount of excess precipitate was independent of time. One can conclude that there is coprecipitation of calcium diliturate on magnesium diliturate and not postprecipitation.

The first two results in Table III show that concentrations of oxalate ion as high as 0.027 M do not interfere with the determination of magnesium. The amount of magnesium found was the same in both cases yet only the second sample contained oxalate ions. This would allow calcium if present in solution, to be separated as the oxalate before the subsequent determination of magnesium as diliturate.

Amounts of magnesium ranging from 1 to 26 mg and with concentrations between 0.1 and 0.5 mg/ml can be determined by precipitation as magnesium diliturate very rapidly and with an error less than 0.5%. The double determination of the hydrated and anhydrous forms allow for better accuracy and at the same time for detection of coprecipitated substances.

THERMOGRAVIMETRIC DETERMINATION OF POTASSIUM WITH DILITURIC ACID

The determination of potassium has always presented a problem since large solubility errors are characteristic of even the most widely used gravimetric methods. More recently colorimetric and spectrophotometric methods have been developed particularly suited for small samples. There is a definite need for an accurate gravimetric method.

When potassium is the only cation present in solution it can be determined as the chloride or the sulfate. The sulfate is also conveniently used for the determination of potassium in organic materials after digestion with sulfuric acid. A number of precipitating agents such as perchlorate, dipicrylaminate, chloroplatinate and 6-chloro-5-nitro-m-toluene sulfonate have been used for the determination of potassium in the presence of small amounts of other metals and alkalies, but in all these determinations caesium and rubidium are also coprecipitated[9].

Dilituric acid has also been used for the determination of potassium. FREDHOLM[4] used it for the qualitative microscopic detection. DE GRAAFF AND NOYONS[6] quantitatively determined potassium, weighing the precipitate after drying at 100°. Their results for quantities of potassium larger than 1 mg were too high while for amounts smaller than 1 mg were erratic. The maximum quantity determined by them was 2 mg. These authors have found that by washing the precipitate with saturated potassium diliturate in 40% ethanol they could obtain values close to theoretical.

It was to examine the conditions of precipitation and to extend the range of po-

tassium concentrations determined that the authors undertook the determination of potassium with dilituric acid.

Experimental

Solutions

Standard potassium chloride solution. A standard solution was prepared from re-crystallized reagent grade KCl dried for two hours at 110°. The potassium concentration was 2.148 mg/ml.

Trimethylamine diliturate solution. As precipitating agent we first tried the dilituric acid solution used for the determination of magnesium, but when this solution proved too dilute we dissolved trimethylamine diliturate in 50% ethanol until saturated. The excess trimethylamine diliturate was filtered off. This solution had a pH of 7 and a concentration around 0.1 M or double that of the dilituric acid solution.

The trimethylamine diliturate was prepared by adding an excess of saturated aqueous solution of dilituric acid to a 1- to 2-% aqueous solution of trimethylamine. The resulting mixture was heated until the precipitate dissolved, and then cooled slowly to 0°. Beautiful large green needles of trimethylamine diliturate precipitated. out of solution. They were filtered and dried in air.

Method of analysis

A 2-ml aliquot of the standard potassium solution was treated with 15 ml of hot trimethylamine diliturate solution. The precipitate was left to form and cool for 1 to 2 h. About 20 min before filtration 5 ml of cold precipitating agent was added, the solution stirred and then cooled in an ice bath. The precipitate was filtered on a sintered glass crucible; once in the crucible it was washed with a saturated potassium diliturate solution in 50% ethanol and finally once with 95% ethanol. The crucible was then placed on the thermobalance thermostated at a temperature ranging from 160° to 230°. The weight of the anhydrous precipitate was obtained within 15 to 20 min.

For different amounts of potassium, proportionate volumes of the trimethylamine diliturate solution were added so as to have a 15- to 20-fold excess of trimethylamine diliturate over potassium.

Results and discussion

In Table IV are results obtained with the above method. The effect of adding the precipitant in one or two portions is shown in Table V.

The trimethylamine diliturate solution was used as the precipitant only after dilituric acid solution was found to be unsatisfactory. Excessively large volumes of the dilituric acid solution were necessary in order to obtain the desired excess of diliturate ions over the potassium ions.

Satisfactory results were obtained only with neutral solutions of the precipitating agent. When the triethylamine diliturate solution was made basic with an excess of trimethylamine the trimethylamine had a tendency to coprecipitate on the potassium salt; on the other hand, if the trimethylamine diliturate solution was made acidic with hydrochloric acid there was incomplete precipitation.

The tendency of potassium diliturate to supersaturate and to form very fine precipitates is very well avoided by two subsequent additions of the trimethylamine diliturate precipitating solution (see Table V).

We have found experimentally from the thermogravimetric curves that 50 to 75 mg of liquid are retained by the filtering crucible (this is an objection to the method of DE GRAAFF where the precipitate was washed solely with saturated potassium dili-turate solution). The glass filter should be as small as possible so as to retain the minimum of wash solution even with a final washing with 95% ethanol.

TABLE IV

THERMOGRAVIMETRIC DETERMINATION OF POTASSIUM WITH DILITURIC ACID

K taken (mg)	K found (mg)	Dev. (mg)
4.29	4.50	+0.21
4.30	4.24	—0.06
3.22	3.16	—0.06
3.01	3.00	—0.01
3.44	3.66	+0.22
2.15	2.05	—0.10
2.15	2.09	—0.06
2.15	2.09	—0.06
2.58	2.25	—0.33
2.15	2.11	—0.04
2.58	2.33	—0.25
1.72	1.52	—0.20
1.72	1.55	—0.17
1.28	1.25	—0.03

TABLE V

METHOD OF PRECIPITATING POTASSIUM DILITURATE

K taken (mg)	K found (mg)	Dev. (mg)	Portions of precipitant
2.15	1.94	—0.21	1 addition
2.15	2.05	—0.10	2 additions
3.22	2.93	—0.29	1 addition
3.22	3.16	—0.06	2 additions

From the data in Table IV it can be seen that the results tend to be low. This method does not eliminate completely the effect of supersaturation, since from calculations on solubility data the negative error is greater than expected. Using the solubility data of REDEMANN AND NIEMANN[3] under our experimental conditions with a dili-turate ion concentration of 0.1 M and an initial concentration of potassium of 0.02 M there would be a negative error of 3%. This gives an error of —0.06 mg for a 2.15-mg sample of potassium. If this correction is made, twelve of the fifteen results have very good agreement with the weight of potassium taken.

We have studied the possibility of determining potassium in the presence of sodium but have found that sodium diliturate coprecipitates even when present in small amounts in spite of the fact that the solubility of the sodium salt is 10 times that of the potassium salt.

Potassium can be determined by precipitation with dilituric acid in the absence

of sodium. Increased accuracy of results is obtained by applying an appropriate solubility correction for potassium diliturate. A determination can be completed in about three hours with an error not exceeding 2%.

PRELIMINARY INVESTIGATION FOR THE THERMOGRAVIMETRIC DETERMINATION OF LEAD WITH DILITURIC ACID

The simplest and best known gravimetric method for the determination of lead weighs the lead as sulfate. The need to correct for the high solubility of lead sulfate, and to heat the precipitate to more than 300° plus an unfavorable gravimetric factor make the use of some other precipitate desirable particularly when the quantity of lead is small. HECHT and coworkers[15] recommend picrolonic acid in such cases. Lead picrolonate washes and filters well, is stable up to 112° but picrolonic acid is an expensive reagent.

It was thought that dilituric acid which is inexpensive would also have the favorable properties possessed by picrolonic acid.

Solutions

Standard lead solution. Recrystallized anhydrous lead nitrate dried in air was weighed, dissolved in water and diluted to volume to yield 0.02-M solutions.

Dilituric acid solution. A 0.02-M solution in 40% ethanol was prepared.

Method of analysis

Dilituric acid solution was slowly added to 25 ml of the 0.02-M lead nitrate solution until there was a 50% excess (molar) of diliturate ions. The precipitate was digested for 30 min on a hot plate, and then left to form for several hours in an ice bath. It was then filtered through a sintered glass filter of medium porosity, washed several times with a 0.001-M solution of dilituric acid in 50% ethanol, and once with 95% ethanol. The glass filter and precipitate were heated in the thermobalance in an atmosphere of CO_2 at the rate of 150°/h and the anhydrous form between 180° and 200°/h.

Analytical results

The results, mostly of a preliminary nature, obtained with the above method are listed in Table VI. Some results obtained when the ratio of diliturate to lead was only slightly above 1 are also recorded in Table VI.

TABLE VI

THERMOGRAVIMETRIC DETERMINATION OF LEAD AS ANHYDROUS LEAD DILITURATE

Pb taken (mg)	Pb found (mg)	Dev. (mg)
Molar ratio of diliturate to lead 1.5/1.0		
42.6	42.3 (anhydrous)	—0.3
42.6	42.5 (anhydrous)	—0.1
51.1	52.1 (hydrate)	+1.0
51.1	52.2 (anhydrous)	+1.4
Molar ratio of diliturate to lead 1.0/1.0		
53.1	49.7 (anhydrous)	—3.4
53.1	49.1 (anhydrous)	—4.0
53.1	49.6 (anhydrous)	—3.5

Discussion of results

Preliminary results using equimolar quantities of lead and dilituric acid gave negative deviations of about 4%. Assuming this is due to the solubility of lead diliturate a K_{sp} value of $4 \cdot 10^{-4}$ was calculated in the 25% ethanol solution at 0°. This is a solubility of 1 mmole of lead diliturate per l. In these calculations it is assumed that there is no supersaturation.

When the ratio of diliturate to lead was increased to 1.5/1.0 the results had a deviation of somewhat less than —0.5%. Digestion of the samples improved the accuracy of the results, as is indicated by the 42.6-mg samples in Table VI.

In a preliminary experiment it was found that the presence of ethanol is essential, since otherwise the precipitate forms only very slowly and incompletely.

Dilituric acid can be used for determining semi-micro amounts of lead in a reasonably short time. One and a half hours for the precipitation and 30 min for the determination of the final weight on the thermobalance.

SUMMARY

The thermolysis curves of magnesium, potassium, and lead diliturate have established that either the hydrated or anhydrous forms of these precipitates are stable enough for their gravimetric use to be possible. Magnesium and lead were determined by precipitation with dilituric acid while potassium was precipitated with trimethylamine diliturate.

RÉSUMÉ

Les courbes de thermolyse des diliturates de potassium, de magnésium et de plomb ont montré que ces composés sont suffisamment stables pour permettre un dosage gravimétrique de ces éléments.

ZUSAMMENFASSUNG

Der Verlauf der thermolytischen Kurven der Diliturate von Kalium, Magnesium und Blei zeigt dass diese Verbindungen sich zur gravimetrischen Bestimmung der erwähnten Elemente eignen.

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THE IDENTIFICATION OF ALIPHATIC AMINES IN AIR AS THEIR BENZAMIDES BY PAPER CHROMATOGRAPHY

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INTRODUCTION

As a portion of a program of the study of individual species in collections from polluted atmospheres, it was felt desirable to develop a method for the separation and identification of aliphatic amines. Several alternative methods were considered[1,2], but in view of experience in our laboratory[3] with the method of DE JONGE[4,5] it was decided that an investigation should be made of the possible use of the benzamides as suitable derivatives for paper chromatography. As has been previously noted[3], it is possible greatly to extend the lower limit of such a technique by the use of ^{14}C labelling.

PROCEDURE

Materials

Chemicals used, except where otherwise noted, were reagent grade, or the purest available. Benzoic acid, labelled with ^{14}C in the carboxyl group, was purchased from Tracer Laboratory. It had a nominal specific activity of 1.46 mC/mm. Benzoyl chloride was prepared from this in the usual way[6].

Lower molecular weight benzamides for calibration purposes were prepared by the SCHOTTEN-BAUMAN reaction[7]. The higher molecular weight derivatives were made by the method of SASIN *et al.*[8].

Schleicher and Schüll papers 2040a gl. and 2045a gl. were used as indicated for the paper chromatographs. Radioautographs were prepared using Eastman Kodak x-ray film, no screen.

DE JONGE's systems are as follows: System M: 80% methanol–cyclohexane; ratio 20:80; System P: 50% ethanol–cyclohexane, ratio 20:80; System E: 20% propanol–cyclohexane, ratio 20:80.

Determination of R_F values

A solution of each pure benzamide containing approximately 2 mg/ml was chromatographed according to the procedure of DE JONGE[4] at 20°. The spots were located in the usual fashion by means of ultraviolet light. The results are tabulated in Table I for DE JONGE's systems M and E. System P was also tried, but found unsatisfactory. Mixtures of benzamides containing approximately 2 mg/ml of each benzamide were found to separate adequately in most cases, as would be anticipated by the R_F values given.

Determination of lower limit of identification

For this purpose, very dilute solutions of the radiocarbon-type benzamides were chromatographed, placed on x-ray film for eight to ten days and the radioautographs developed in the usual way. The lower limit of identification was found to be approxi- mately 2.5 μg of each benzamide. Quantitative measurements could be made on larger amounts by elution according to De Jonge and Verhage[5] and by a measurement of the absorbance at 225 mμ with a Beckman spectrophotometer, Model DU.

Fig. 1. Radioautograph illustrating separation of even straight chain mixtures of N-benzamides.

Preparation of air samples

Samples of airborne particulate matter collected on glass fiber filters were supplied by the National Air Sampling Network, U. S. Public Health Service. A quantity of filter bearing 3 to 8 g of particulate matter was chopped into small squares, dampened with sodium hydroxide, and extracted with three 250-ml portions of anhydrous

redistilled ether by shaking. Since it was found that all of the amines were removed from a mixture of amine salts in two ether extractions of 20 min each, by reacting the extract with benzoyl chloride, it was assumed that a total extraction time of 11–12 h with ether and sodium hydroxide was sufficient to remove any amines from the particulate matter. After this interval the extract was decanted through a filter and acidified with hydrogen chloride gas. The volume of extract was reduced to approximately 50 ml by means of an air stream. A slight excess of 10% sodium

Fig. 2. Radioautograph of odd mixtures of straight chain N-benzamides.

hydroxide and 0.1 to 0.15 ml of radioactive benzoyl chloride were added, and the reaction mixture was shaken for 20 min. The benzamides were extracted with three portions of benzene, to make a total volume of approximately 40 ml. The benzene solution was evaporated in an air stream to a volume of 2–3 ml, diluted to 5 ml with additional benzene, and chromatographed as described above.

Atmospheric vapors were collected in approximately 10% sulfuric acid by means of a Smith-Greenburg impinger. The collected sample was neutralized with sodium hydroxide in a closed flask with a sidearm dipping into a container of ether. This trapped any vapor liberated during the neutralization. The aqueous layer was then extracted with ether, the ether layers were combined, and were treated as indicated above for the particulate matter.

RESULTS AND DISCUSSION

The data in Table I gives a survey of mean R_F values of the benzamides. These values are not to be taken as absolute, since they are influenced by some of the usual factors which cause variation in R_F values. The presence of foreign material as are found in air samples tend to depress the values still more.

Homologous benzamides are separated satisfactorily on Schleicher and Schüll 2040a gl. paper with a development time of 3 h, while isomeric benzamides, with the exception of the pair N-propyl and N-isopropyl, are not completely separated. Although the pair N-decyl and N-dodecyl benzamides are incompletely separated on S. & S. 2040a gl. paper in the standard development time, these are very satisfactorily separated on S. & S. 2045a gl. paper.

While secondary benzamides are separated from each other, they are not completely separated from some of the primary benzamides, so that spectra must be relied upon to differentiate them[9].

A typical separation of a mixture of N-ethyl, N-sec-butyl, N-hexyl, N-octyl, and

TABLE I

N-BENZAMIDES

R_F value $\times$ 100

N-Benzamide	System M	System E
S & S 2040a gl. paper		
N-methyl	3.60	4.49
N-ethyl	8.35	16.68
N-propyl	16.11	30.59
N-isopropyl	22.13	41.50
N-sec-butyl	33.75	58.29
N-isobutyl	29.63	61.87
N-*n*-butyl	33.90	
N-isoamyl	42.82	68.96
N-hexyl	62.62	82.28
N-heptyl	71.19	
N-octyl	81.82	
N-decyl	87.03	
N-dodecyl	89.30	
2-ethyl-N-hexyl	80.83	95.68
1,3-dimethyl-N-butyl	65.31	81.89
benzoic acid	16.0–19.43	44.18
N,N-diisopropyl	84.13	
N,N-diisobutyl	92.69	
S & S 2045a gl. paper		
N-decyl	75.37	
N-dodecyl	82.02	

TABLE II

N-BENZAMIDES FOUND IN AIR SAMPLES

Sample	Benzamide found	mg Benzamide	Amine mg	Total air flow m³	Amine mg/m³ air
Los Angeles	N-ethyl	3.045	0.920	1,800	5.1·10⁻⁵ a
Birmingham	None[b]	less than identifiable quantity		25,167	—
New York	N-methyl	3.516	0.808	5.44	0.149

The air flow is estimated as an average of 2000 m³ per 24 h in the absence of specific air flow
data.
No individual benzamide could be identified.
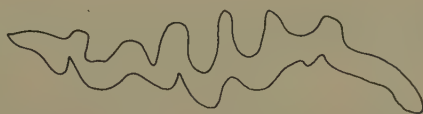
Fig. 3. Radioautograph of atmospheric vapors, New York City.

N-decyl benzamides is illustrated in Fig. 1, with the quantities increasing from 15 to
50 μg, while in Fig. 2 is illustrated a separation of N-methyl, N-propyl, N-isoamyl,
and N-heptyl benzamides of the same magnitude.

A radioautograph of an air particulate sample from Los Angeles, California showed
two distinct spots at R_F values corresponding to N-ethyl and possibly N-propyl benz-
amide plus benzoic acid. By rechromatographing these areas in system E they have
been shown to be N-ethyl benzamide, and benzoic acid formed by the hydrolysis of
benzoyl chloride. A larger area near the front of the chromatogram was produced by a
yellowish material which gave a reddish fluorescence under ultraviolet light.

A similar radioautograph of air particulate matter from Birmingham, Ala., showed no such spots other than benzoic acid and the large frontal smear.

Fig. 3 is a representation of a chromatogram of a sample of atmospheric vapor collected in approximately 10% H_2SO_4 in a New York City fish market. Two distinct spots are visible at R_F values corresponding to N-methyl benzamide and the expected benzoic acid area. The approximate values of the benzamides found in both the Los Angeles and the New York sample can be seen in Table II. These have been estimated by a modification of the isotope dilution method[10] and by spectrophotometry.

SUMMARY

A method is described for the separation of amines as their benzamides by paper chromatography. Data are given on separations in two systems. Homologous benzamides from C_1 to C_{10} are best separated on S & S 2040a paper while C_{10} and C_{12} are separated on 2045a paper. When radio carbon labelled benzamides were chromatographed and placed on x-ray film for eight to ten days with subsequent development of the radioautograph, the lower limit of identification was found to be ca. 2.5 μg of each benzamide. The results of analysis for amines in two samples of air particulate matter, and one of atmospheric vapors are presented.

RÉSUMÉ

Une méthode chromatographique et radiochimique est décrite pour la séparation et l'identification des amines aliphatiques contenues dans l'air.

ZUSAMMENFASSUNG

Beschreibung einer papierchromatographischen und radiochemischen Methode zur Trennung und Bestimmung von aliphatischen Amine in der Atmosphäre.

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SPECTROPHOTOMETRIC DETERMINATION OF PALLADIUM(II) WITH 5(p-DIMETHYLAMINOBENZYLIDENE)RHODANINE*

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n 1928 FEIGL[1] reported that rhodanine and many of its derivatives gave precipi-ates with silver ion and mercuric ion, and that 5(p-dimethylaminobenzylidene)rho-danine (hereinafter designated DMABR for brevity) was especially suitable as a ensitive, specific reagent for silver. In a study of spot test methods for the noble metals, HOLZER[2] reported that DMABR was a sensitive reagent for silver, gold, platinum, and palladium; depending upon the concentration of the metal in solution, he spot from palladium was bright red-violet to black-violet, and was reported to be readily distinguishable from the color produced by the other elements. FEIGL, KRUMHOLZ AND RAJMANN[3] used DMABR for the detection of silver, gold, and palla-dium; palladium salts gave a violet precipitate, and platinum and iridium also gave positive tests with the reagent, but not as readily. Osmium, rhodium, and ruthenium were reported to give no reaction. The limit of detection of palladium, in 0.1 N hydrochloric acid solution, was given as 0.66 μg in solution and 0.01 μg on spot test paper.

The purpose of the present investigation was to develop a spectrophotometric method for palladium using DMABR reagent, and to endeavor to determine the nature of the color reaction.

APPARATUS

Spectral curves were recorded with a Beckman Model DK-1 spectrophotometer. A Beckman Model DU spectrophotometer was used for making more precise absorbance measurements at a given wave length. Matched silica cells of 1.00-cm optical path were used. The instruments were located in a constant temperature room (26°) and no further attempt was made to control the temperature of the solutions measured.

Measurements of pH were made with a Beckman Model H-2 pH meter, using glass and calomel electrodes.

Calibrated weights and calibrated volumetric ware were used.

REAGENTS

Standard palladium solution

Exactly 0.5000 g of palladium metal powder (A. D. Mackay, Inc.) was dissolved

in aqua regia. The solution was evaporated twice with hydrochloric acid to destro[
nitric acid; the residual solution, having a volume of about 45 ml, was diluted wit[
water to 500 ml (volumetric flask). This stock solution, 1000 p.p.m. in palladium an[
about 0.5 N in hydrochloric acid, was assayed by precipitation and weighing a[
palladium dimethylglyoximate[4]. The palladium found in triplicate 20.00-ml aliquo[
was 19.95, 19.94, and 19.95 mg. Working solutions were prepared as needed b[
volumetric dilution of the stock solution.

DMABR

The 5(p-dimethylaminobenzylidene)rhodanine (Eastman No. 2748) was used a[
received. Two different lots gave slight differences in absorbance and in wave leng[
of absorption maximum of the developed palladium solution; recalibration is therefo[
indicated when a different lot of reagent is put into use. Preliminary tests showed th[
the reagent was more soluble and also more stable in formic acid than in ethan[
acetic acid, or hydrochloric acid. The reagent stock solution was prepared quantit[
tively by dissolving a known weight of the solid DMABR in 88% formic acid; workin[
solutions were prepared by volumetric dilution. The stock solution was stable for [
least 2 months.

Organic acids

Formic acid (88%) and glacial acetic acid (99.7%) were analytical reagent grad[
Propionic acid was Eastman No. 396, b.p. 141–143°.

Other reagents

Substances used in interference tests were obtained as or prepared from reage[
quality chemicals. Chlorides of iron(III), cobalt(II), nickel(II), chromium(II[
copper(II), mercury(II), rhodium(III), iridium(III) and ruthenium(III) were use[
as sources of the respective metal ions, and potassium dichromate was used f[
chromium(VI). Solutions of gold(III) and platinum(IV) were prepared from the pu[
metals by dissolution in aqua regia and repeated evaporation with hydrochloric aci[
Osmium tetroxide was dissolved in sodium hydroxide solution, which was then acid[
fied with hydrochloric acid. Sodium or potassium salts were used as sources for th[
anions.

<div align="center">EXPERIMENTAL</div>

Preliminary experiments

The red to violet precipitate formed in neutral or slightly acidic solution wi[
DMABR in ethyl alcohol is a sensitive spot test for palladium[2]. The principal proble[
in using this reaction as a spectrophotometric method was to find a condition and[
solvent to prevent the formation of the precipitate. In solution buffered at pH [
palladium (1–4 p.p.m.) and DMABR in ethyl alcohol gave a red-violet solution havi[
an absorption maximum at 480 mμ. However, within a few minutes a red turbidi[
developed; similar precipitates were obtained at higher pH, up to pH 10. N,N-dimeth[
formamide was effective in preventing precipitation, but the absorption maximu[
varied from 480 to 515 mμ, depending upon the amount of solvent used, and absor[
ances were not well reproducible. In addition, the reagent blank in N,N-dimeth[
formamide (orange solution) showed extensive absorption in the same region as t[

palladium product, and the reagent solution in N,N-dimethylformamide was stable for only a few days. Preparations in formic, hydrochloric, acetic, or propionic acid medium were more soluble and more stable, and these systems were investigated in detail.

Formic acid solutions

The influence of each different variable was evaluated singly by maintaining other factors constant. Solutions of the reactants were mixed to a final volume of 10.0 ml; after allowing 10 min for color development the absorbance was measured at the absorption maximum of 515 mμ.

Concentration of DMABR

3 ml of 0.10 N hydrochloric acid containing 10 μg of palladium was mixed with 1.0 ml to 5.0 ml of 0.01% DMABR in 44% formic acid and 6.0 to 2.0 ml of 44% formic acid. The absorbance increased only slightly with the amount of DMABR, reaching a maximum of 0.412 at 3.0 and 4.0 ml of the reagent solution.

Formic acid concentration

1 ml of solution containing 10 μg of palladium and 1.0 ml of 0.04% DMABR (in 44% formic acid) were mixed with 1.0 to 5.0 ml of 88% formic acid and 7.0 to 3.0 ml of water. Absorbance measurements were as follows:

ml of 88% formic acid:	1.0	2.0	3.0	4.0	5.0
ml of water:	7.0	6.0	5.0	4.0	3.0
absorbance at 515 mμ:	ppt.	0.423	0.438	0.183	0.015

Hydrochloric acid concentration

1 ml of solution containing 10 μg of palladium and 4.0 ml of 0.01% DMABR in 44% formic acid were mixed with 0.0 to 4.0 ml of 0.10 N hydrochloric acid and 5.0 to 1.0 ml of water. Absorbance measurements were as follows:

ml of 0.10 N HCl:	0	1.0	2.0	3.0	4.0
ml of water:	5.0	4.0	3.0	2.0	1.0
absorbance at 515 mμ:	0.435	0.415	0.405	0.388	0.322

Solutions containing 2.0 or 3.0 ml of 0.10 N hydrochloric acid attained maximum absorbance most rapidly, and were more stable against precipitation than solutions of lower or of higher acid concentration.

Procedure

Transfer 3.0 ml of 0.10 N hydrochloric acid containing 5 to 25 μg of palladium to a dry 10-ml volumetric flask; add 3.0 ml of 88% formic acid, 1.0 ml of DMABR reagent (0.04% solution in 44% formic acid); dilute to volume with water. Allow 7 to 10 min for color development, then measure the absorbance at 515 mμ against a reagent blank.

The system conforms to Beer's law, as shown by the data in Table I. The specific

absorptivity, 0.406 per p.p.m.–cm, corresponds to a palladium absorptivity of $4.32 \cdot 10^4$ l mole^{-1}cm^{-1}.

TABLE I

CALIBRATION DATA

Pd conc., p.p.m.	In formic acid		In hydrochloric acid		In propionic acid	
	Absorbance at 515 mμ	Absorptivity, p.p.m.$^{-1}$ cm^{-1}	Absorbance at 515 mμ	Absorptivity p.p.m.$^{-1}$ cm^{-1}	Absorbance at 530 mμ	Absorptivity, p.p.m.$^{-1}$ cm^{-1}
0.50	0.210	0.420	0.205	0.410	0.187	0.374
1.0	0.407	0.407	0.399	0.399	0.378	0.378
1.5	0.603	0.402	0.583	0.389	0.567	0.378
2.0	0.802	0.401	0.785	0.393	0.763	0.381
2.5	1.000	0.400	0.970	0.388	0.963	0.385
Average:		0.406		0.396		0.379
Average deviation:		0.006		0.007		0.003

Hydrochloric acid solutions

The same general procedure was used as with the formic acid solutions, for evaluating the influence of the variables. The absorption maximum occurred at 515 mμ.

Effect of hydrochloric acid concentration

1 ml of solution containing 10 μg of palladium was mixed with 3.0 ml of DMABR reagent solution, then was diluted to 10.0 ml with hydrochloric acid of different concentrations. Absorbance measurements were as follows:

HCl for dilution, N:	0.10	0.20	0.40	0.60	0.80
absorbance at 515 mμ:	0.400	0.370	0.327	0.200	0.033

At the two lowest acidities, maximum color development occurred almost immediately, and the absorbance was constant for about 45 min, after which it decreased slowly. At the higher acidities the initial absorbance decreased with increasing acid concentration, and the absorbance gradually increased with time, up to one hour (after which the measurements were discontinued).

Substitution of formic acid solution for part of the hydrochloric acid for dilution to volume decreased the absorbance, and increased the time required for full color development.

Procedure

Transfer 1.0 ml of solution containing 5 to 25 μg of palladium to a dry 10-ml volumetric flask; add 3.0 ml of DMABR reagent, and dilute to volume with 0.10 N hydrochloric acid. Measure the absorbance at 515 mμ against a reagent blank.

The data of Table I show that the system conforms to Beer's law; the average specific absorptivity is 0.396 per p.p.m.–cm. Solutions containing 0.50 p.p.m. of palladium were stable for about 45 min; the stability decreased with increasing palladium concentration, so that at 3.0 p.p.m. the absorbance was constant for less than 10 min. Eventually a dark red precipitate separated from all samples. The precision was tested by 10 preparations containing 1.0 p.p.m. of palladium in the final solution; the average absorbance was 0.399 ± 0.007.

Acetic acid solutions

When glacial acetic acid was used as the diluent, the absorption maximum occurred at 530 mμ. Although the system conformed to Beer's law and the reproducibility was satisfactory, the sensitivity for palladium was much lower than in other media; the specific absorptivity was only 0.052 per p.p.m.–cm. Samples required about 30 min for full color development, and the solutions were stable for about one hour.

Propionic acid solutions

Procedure

This procedure was adopted after a preliminary study of the variables. To a dry 10-ml volumetric flask transfer 2.0 ml of 0.05 N hydrochloric acid containing 5 to 25 μg of palladium. Add 1.0 ml of DMABR reagent (0.04% solution in 88% formic acid) and mix thoroughly. (A red-violet precipitate forms immediately; it is readily soluble in propionic acid). Dilute almost to volume with propionic acid and mix thoroughly; temperature and volume decrease on mixing. Bring the mixture to room temperature, and complete the dilution to volume with propionic acid. Prepare a corresponding blank. Allow 15 min for full color development and measure the absorbance at 530 mμ, the absorption maximum.
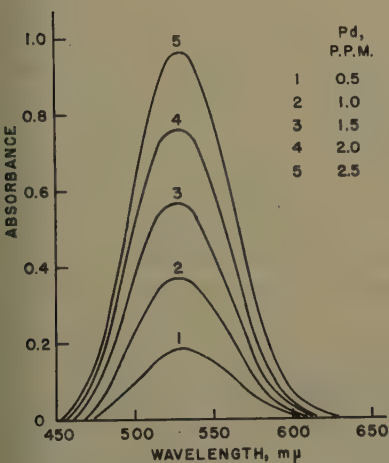
Fig. 1. Palladium–DMABR system in propionic acid solution.
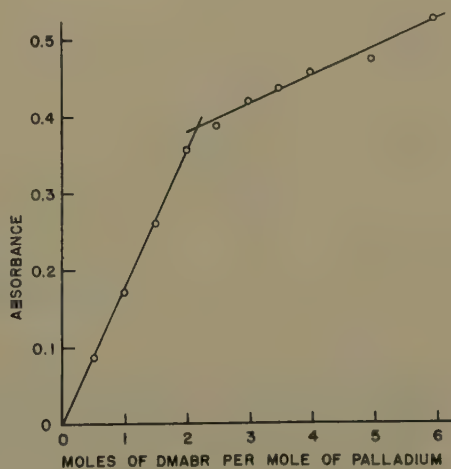
Fig. 2. Mole ratio plot for palladium–DMABR system.

The absorption spectra for several concentrations of palladium are shown in Fig. 1. The system conforms to Beer's law, as shown by data in Table I. The specific absorptivity of 0.379 per p.p.m.–cm corresponds to a palladium absorptivity of $4.03 \cdot 10^4$ l mole^{-1} cm^{-1}.

Stability

The solutions showed constant absorbance for at least two hours, then faded slowly over a period of 24 h (measurements were not continued beyond this time). No precipitate appeared even after several days.

Effect of foreign ions

Solutions containing 1.0 p.p.m. of palladium and varying amounts of diverse ions
were color-developed and measured by the standard procedure. The tolerance for a
foreign ion was taken as the largest amount of the ion that could be present with the
palladium and give a transmittance within 0.4% (absolute) of that of the palladium
alone; at the 1.0 p.p.m. palladium level a difference of 0.4% transmittance corresponds
to an absorbance difference of about 0.005. Interference tests were made in both the
hydrochloric acid and the propionic acid solution. The results are summarized in
Table II.

TABLE II
EFFECT OF FOREIGN IONS
Palladium concentration, 1.0 p.p.m.

Foreign ion	Tolerance, in p.p.m.	
	Hydrochloric acid solution	Propionic acid solution
Platinum(IV)	200	20[a]
Rhodium(III)	10	300
Iridium(III)	20	10
Ruthenium(III)	10	20
Osmium(IV)	100	100
Gold(III)	0	0
Iron(III)	50	10
Cobalt(II)	200	300
Nickel(II)	100	300
Chromium(III)	300	
Chromium(VI)		2
Copper(II)		5
Mercury(II)		100
Nitrate		> 200
Sulfate		> 300

[a] This tolerance applies only if absorbance is measured within 15 min; platinum(IV) slowly
develops a red solution which absorbs strongly at 525–530 mμ.

By the method reported here for palladium, silver ion is precipitated as silver chlo-
ride; however, the amount of silver ion remaining in solution saturated with silver
chloride is sufficient to give the characteristic color with DMABR. Preliminary tests
have shown that the violet color formed by reaction of DMABR with gold(III) could
be used as a spectrophotometric method for the latter in the concentration range of
a few p.p.m.

COMPOSITION OF THE REACTION PRODUCT

The stoichiometry of the palladium–DMABR reaction was investigated spectrophoto-
metrically by the mole ratio method[5], the method of continuous variations[6], and the
slope ratio method[7]. The precipitate formed by the reaction was also subjected to
elemental analysis.

Mole ratio method

A series of solutions was prepared from a constant amount of palladium ($1.0 \cdot 10^{-7}$
mole) and varied amounts of DMABR ($0.5–7.0 \cdot 10^{-7}$ mole). 3 ml of palladium solution
(in 0.1 N hydrochloric acid) and 3 ml of DMABR solution were diluted to 10.0 ml

with 0.10 N hydrochloric acid. Absorbances were measured at several wave lengths around the absorbance maximum. Plots of absorbance (at a given wave length) against the mole ratio of DMABR to palladium showed a distinct change of slope at a 2 : 1 ratio. Solutions of the DMABR reagent in formic–hydrochloric acid show a considerable absorbance in the same region as the absorbance maximum of the DMABR–palladium product. The absorbances of DMABR solutions of various concentrations were measured against a formic–hydrochloric acid blank. The data for the DMABR–palladium solutions were corrected for the absorbance due to unreacted DMABR in excess of the 2 : 1 ratio to palladium; the break in the absorbance vs. mole ratio plot was thereby sharpened. The plot was also linear, after the break at the 2 : 1 mole ratio, up to at least a 7 : 1 mole ratio, indicating the 2 : 1 product as the only (absorbing) reaction product formed.

The experiments were repeated with solutions diluted with propionic acid instead of with hydrochloric acid. The absorbance vs. mole ratio plots again showed sharp breaks at a 2 : 1 mole ratio of DMABR to palladium. A typical plot is shown in Fig. 2.

Continuous variations method

The palladium solution was $2.0 \cdot 10^{-4}$ M, in 0.10 N hydrochloric acid; the DMABR, also $2.0 \cdot 10^{-4}$ M, was in 88% formic acid solution. The solutions were mixed in the ratio of x ml of DMABR to $5.0 - x$ ml of palladium, and were then diluted to 50 ml with 88% formic acid and 0.10 N hydrochloric acid in such proportion that these acids would be present in the same amounts in all samples. Absorbance was measured at several wave lengths around the absorbance maximum. The absorbance data were corrected for any excess DMABR or excess palladium, assuming a 2 : 1 reaction ratio as indicated by the mole ratio study. A plot of absorbance against mole fraction of DMABR showed a sharp maximum at a mole fraction of 0.67, representing a 2 : 1 mole ratio of DMABR to palladium in the color reaction.

The same results were obtained with solutions in which the reactants were diluted with propionic acid. A typical continuous variations plot is shown in Fig. 3.

Slope ratio method

In one series of solutions the amount of DMABR was kept constant ($6.0 \cdot 10^{-7}$ mole) and large with respect to the varying amounts of palladium ($0.5 - 2.0 \cdot 10^{-7}$ mole). In the second series the amount of palladium was kept constant and equal to the concentration of the DMABR in the first series, and the amount of DMABR reagent was varied from $0.5 - 2.0 \cdot 10^{-7}$ mole. The reactants were diluted to volume with propionic acid. The plot of absorbance against concentration of the variable component is shown in Fig. 4; the right-hand ordinate scale has been displaced downward by the amount of the absorbance of the DMABR solution alone; in this way the origins of the two curves coincide, and the ratio of their slopes is more readily apparent. The ratio of the slopes of the two curves is very nearly 2 : 1, again confirming the 2 : 1 reaction ratio of DMABR to palladium.

Elemental analysis

Palladium(II) solution (200 mg in 200 ml) was precipitated by dropwise addition of 1% DMABR solution (in formic acid). After standing overnight the precipitate

was further settled by centrifugation. The supernatant solution was removed and the precipitate was washed repeatedly with 95% alcohol, after which it was dried in a vacuum desiccator over anhydrous magnesium perchlorate. Flaky, red-violet crystals were obtained. (Attempts to recrystallize the product from formic acid resulted in an apparently amorphous mass). Different preparations were submitted to each of two different analytical laboratories for elemental analysis. The results for carbon, hydrogen, nitrogen, and sulfur were in such poor agreement as to be of no value in trying to deduce the stoichiometric composition of the precipitate. Obviously, the precipitate was not pure, probably as a result of absorption and/or solvation in the preparation, and no further attempt was made along this line.
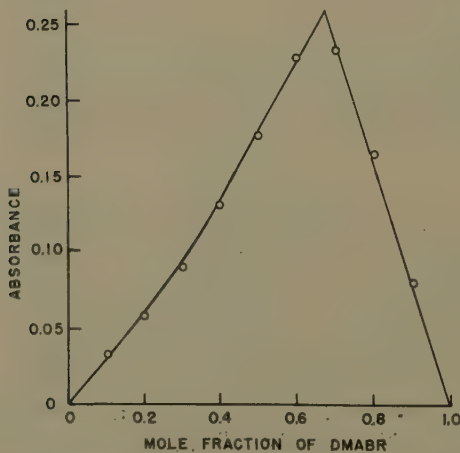
Fig. 3. Continuous variations plot for palladium–DMABR system.
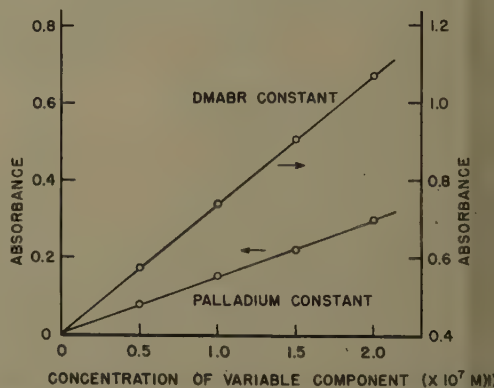
Fig. 4. Slope ratio plot for palladium–DMABR system.

DISCUSSION

The method reported here compares favorably in sensitivity with other spectrophotometric methods for palladium; a summary of several methods has been given by AYRES AND ALSOP[4].

The reaction of rhodanine (I) and its derivatives, including 5(p-dimethylaminobenzylidene)rhodanine (II),
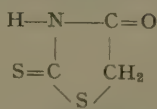
I. Rhodanine
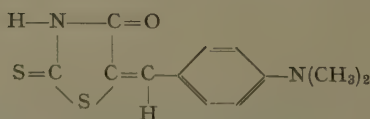
II. 5(p-dimethylaminobenzylidene)-rhodanine (DMABR)

with various metal ions has been studied extensively[2,3,8-11]. Deductions from these studies lead to the conclusion that the $=N-C-S-$ group is probably responsible

for reactions with metal ions. The nitrogen and sulfur atoms in this group are capable of acting as electron-pair donors. If DMABR acts as a bidentate coordinator and in a 2 : 1 mole ratio with palladium, as was found experimentally by the spectrophoto-

netric methods, a complex ion of the empirical formula $[Pd(DMABR)_2]^{+2}$ might be
ormed. Three different structures would be possible, depending upon which of the
atoms of the $=N{-}C{-}S{-}$ group served as electron-pair donors, but each of these
$\qquad\qquad\quad \overset{\|}{S}$
oossible structures would involve a 4-membered ring having considerable strain. It
eems likely, also, that there would be steric effects operating against the formation of
uch structures. If the reactants form a complex ion as postulated above, the precipi-
ate formed might be represented by $Pd(DMABR)_2X_2$, in which X represents a uni-
valent anion such as chloride, formate, or propionate. Test for chloride, after sodium
usion of the precipitate, was negative, as was also a test for formate and propionate
with chromotropic acid, after dissolution of the precipitate in sulfuric acid.

SUMMARY

A sensitive spectrophotometric method has been developed for the determination of palladium,
using 5(p-dimethylaminobenzylidene)rhodanine reagent in formic, hydrochloric, or propionic acid
solution. The systems conform to Beer's law. The specific absorptivity is in the range 0.38 to 0.40
per p.p.m.–cm in the different solvents. The optimum range for 1.00-cm optical path is about
0.4 to 2.5 p.p.m. of palladium. At higher concentrations of palladium a violet-red precipitate
forms within a few minutes. In propionic acid solution maximum color is attained at room temper-
ature in 10 to 15 min, and is stable for more than two hours. The system is somewhat sensitive
to hydrogen ion concentration; maximum absorbance and stability are attained at 0.01 N hydro-
chloric acid in the final solution. Platinum(IV), ruthenium(III), iridium(III), iron(III), chromium-
(VI), and copper(II) interfere if present in amounts several times greater than the amount of
palladium; gold(III) interferes very extensively. The mole ratio method, the continuous variations
method, and the slope ratio method all show the mole ratio of DMABR to palladium to be 2 : 1
in the color-forming reaction.

RÉSUMÉ

Une méthode spectrophotométrique sensible est proposée pour le dosage du palladium, au moyen
de p-diméthylaminobenzylidènerhodanine. Le dosage s'effectue en milieu formique, chlorhydrique
ou propionique. Il convient pour des teneurs en palladium de 0.4 à 2.5 p.p.m.; à des concentrations
plus élevées, il y a formation d'un précipité violet.

ZUSAMMENFASSUNG

Beschreibung einer empfindlichen spektrophotometrischen Methode zur Bestimmung von Palla-
dium mit Hilfe von p-Dimethylaminobenzylidenrhodanin in salzsaurer-, ameisensaurer oder pro-
pionsaurer Lösung. Der geeignete Konzentrationsbereich liegt zwischen 0.4 und 2.5 p.p.m.; bei
höheren Konzentrationen an Palladium entsteht nach wenigen Minuten ein rotvioletter Nieder-
schlag.

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IDENTIFICATION OF PHOSPHATE ANIONS IN NIOBIUM AND TANTALUM PHOSPHATES BY MEANS OF INFRA-RED SPECTRA

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The infra-red absorption spectra of many inorganic compounds have been studied recently, and methods have been devised for the identification and even the determination of many substances. Compilations of infra-red spectra have been published by MILLER AND WILKINS[1] and by HUNT et al.[2,3]. MILLER AND WILKINS recorded the spectra of a few orthophosphates but the most important contribution to infra-red studies of solid metal phosphates was made by CORBRIDGE AND LOWE[4]. Many of the observed bands in the infra-red region prove to be due to phosphate anions and arise from stretching vibrations in phosphorus–oxygen bonds. These bands are, as expected, quite different in solids containing orthophosphate, pyrophosphate, and polyphosphate anions, and infra-red examination apparently provides a direct experimental means of identifying the type of anion present in a solid phosphate. With the standard information of CORBRIDGE AND LOWE[4] as a basis, infra-red examination of some niobium and tantalum phosphates and also zirconium pyrophosphate was undertaken in the hope of establishing the types of phosphate anion present in them.

EXPERIMENTAL

Apparatus and techniques

The absorption spectra were recorded on a Perkin-Elmer Model 21, double beam instrument in which a rock-salt prism was used. All spectra were recorded over the wave-number range 600–4000 cm^{-1}. The conventional method of "mulling" the finely powdered specimens in "Nujol", developed by KELLER AND PICKETT[5], was employed since the absorption bands of "Nujol" did not interfere with the characteristic phosphate bands in the region 650–1350 cm^{-1}. Sodium chloride disks were used to contain the mulls.

Reference substances

Magnesium pyrophosphate was prepared by igniting magnesium ammonium phosphate. Disodium hydrogen phosphate was the commercially available material of "AnalaR" grade; this was also used to prepare sodium orthophosphate by the method of HALL[6], and to prepare sodium triphosphate by the method of AUDRIETH[7].

Infra-red spectra of these reference substances were found to be in good agreement with those recorded by CORBRIDGE AND LOWE[4].

Results

Infra-red spectra of niobium phosphate ($Nb_2O_5 \cdot 2\ P_2O_5$), magnesium pyrophosphate ($Mg_2P_2O_7$) and zirconium pyrophosphate (ZrP_2O_7) are shown in Fig. 1. The absorption peaks are listed in Table I, the wave number being given in cm^{-1}.
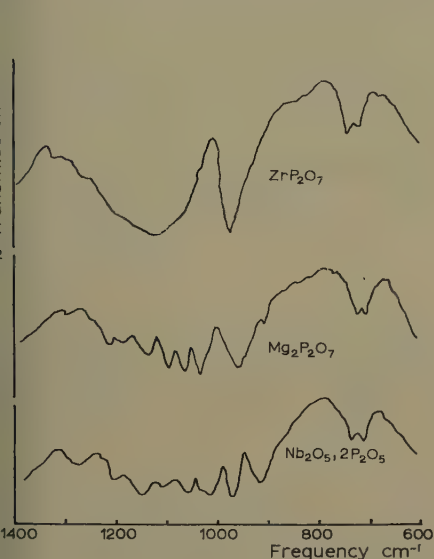

Fig. 1.

Fig. 2.

TABLE I

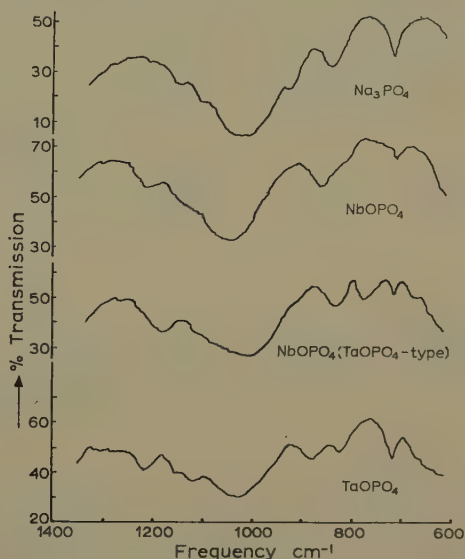| $Nb_2O_5 \cdot 2\ P_2O_5$		ZrP_2O_7		$Mg_2P_2O_7$ (found)		$Mg_2P_2O_7$ (Corbridge and Lowe)	
715	s	720	s	710	s		
730	w	740	w	725	w	725	m
915	vs	975	vs	910	w	907	m
975	s	1075 to 1125	sb	970	sb	932	m
1015	m			1045	m	1008	w
1055	w			1065	m	1049	m
1125	w			1100	w		
		1155	w				
1155	m			1130	m	1122	vs
1210	w			1205	m	1161	vs

vs = very strong, s = strong, m = medium, w = weak and b = broad

TABLE II

$NbOPO_4$		$TaOPO_4$		$NbOPO_4$ ($TaOPO_4$ structure type)		Na_3PO_4 (found)		Na_3PO_4 (Corbridge and Lowe)	
860	mb	825	m	772	m	845	sb	914	ww
1025 to 1065	vsb	860	mb	830	s	930	w		
1150	w	1010 to 1060	vsb	990 to 1050	vsb	985 to 1070	vsb	1028 to 1125	vsb sb
1210	w	1110	w	1175	m	1150	w		
		1210	m						

Infra-red spectra of $NbOPO_4$, $TaOPO_4$, $NbOPO_4$ (structure type $TaOPO_4$) and Na_3PO_4 are reproduced in Fig. 2. The absorption bands are listed in Table II.

The infra-red specimen of $Ta_2O_5 \cdot 3P_2O_5$ (TaP_3O_{10}) is compared with that of Na_5P_3 O_{10} (phase II) in Fig. 3. Absorption peaks are given in Table III.
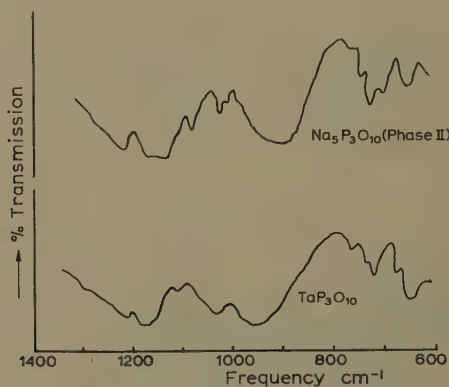
Fig. 3.

TABLE III

TaP_3O_{10}		$Na_5P_3O_{10}$(phase II) (found)		$Na_5P_3O_{10}$(phase II) (Corbridge and Lowe)	
655	m	655	m	665	s
725	s	715	w	737	m
760	w	730	m	906	vsb
930 to 975	vsb	745	w		
		890	sb	1016	w
1040	w	1010 to 1025	w	1098	s
1110	ww			1145	vs
1060 to 1175	vsb	1095	m	1165	s
1210	w	1145 to 1165	vsb	1184	s
		1215	m	1214	s

DISCUSSION

It was pointed out by CORBRIDGE AND LOWE[4] that the spectra of solid samples are liable to be influenced by a number of factors which are less important in pure liquid and liquid solutions. Absorption bands due to particular groups can be broadened, split, or shifted by interaction with other units in the structure (adjacent ions, water molecules, etc.) or by hydrogen bonding.

If the spectra of $Nb_2O_5 \cdot 2P_2O_5$, ZrP_2O_7 and $Mg_2P_2O_7$ are compared (Fig. 1), it is evident that whereas ZrP_2O_7 gives a simple spectrum the spectra of $Nb_2O_5 \cdot 2P_2O_5$ and $Mg_2P_2O_7$ are characterised by a large number of splittings; slight shifting of the

bands is apparent also. The general pattern, however, remains the same, and the presence of $P_2O_7^{-4}$ groups in all three structures appears likely.

In Fig. 2, the niobium and tantalum phosphates show very little splitting, but the broad band is somewhat displaced from the position in which it occurs in Na_3PO_4. The spectrum of tetragonal $NbOPO_4$ resembles more closely that of Na_3PO_4, whereas the spectra of $TaOPO_4$ and isomorphous $NbOPO_4$ are again similar. All these compounds show the general absorption pattern characteristic of PO_4^{-3} groups. It appears, therefore, that these substances are correctly regarded as orthophosphates. Polymerised phosphate anions in the niobium and tantalum salts would introduce absorption differences much greater than those indicated in Fig. 2.

The compound $Ta_2O_5 \cdot 3\ P_2O_5$ appears to be a true triphosphate, since it gives a spectrum (Fig. 3) closely related to that of sodium triphosphate (phase II) containing $P_3O_{10}^{-5}$ groups.

SUMMARY

Some niobium and tantalum phosphates have been prepared and their infra-red spectra have been recorded and compared with those of reference substances. It has been possible to identify PO_4^{-3}, $P_2O_7^{-4}$ and possibly $P_3O_{10}^{-5}$ groups in different samples of niobium and tantalum phosphates.

RÉSUMÉ

Quelques phosphates de niobium et de tantale ont été préparés. Les spectres infra-rouge obtenus avec ces composés ont permis d'identifier les groupements PO_4^{-3}, $P_2O_7^{-4}$ et $P_3O_{10}^{-5}$.

ZUSAMMENFASSUNG

Es wurden die Infrarot Spektren einer Anzahl von Niob- und Tantalphosphaten aufgenommen und mit denen von Magnesium- und Natriumphosphaten verglichen, wobei PO_4^{-3}, $P_2O_7^{-4}$ und wahrscheinlich $P_3O_{10}^{-5}$ Gruppen nachgewiesen werden konnten.

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MECHANISM OF ELEMENTAL SPECTRAL EXCITATION IN FLAME PHOTOMETRY

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INTRODUCTION

In the course of studying flame photometry in high temperature flames (oxy–cyanogen, 5000°) and low temperature flames (oxy–hydrogen, 3000°), several interesting observations were made which are not explained by current interpretation of flame spectra. These were as follows:

(1) The flame acts as a U.V. source. The intensity of metal spectra increases with increased U.V. radiation from the flame, even when the temperature of the flame decreases.

(2) In oxy–hydrogen flames, metal spectral lines with wavelengths significantly less than 2800 Å are not usually observed.

(3) Organic solvents increase the spectral intensity many-fold.

Current theory leads us to believe that flame temperature is the main variable in controlling spectral intensity. Although it explains qualitatively the third of these observations, it does not explain the first two. In an effort to understand these phenomena, the following postulations were made: (1) Metal atoms are excited by ultraviolet light in the flame. (2) The metal must attain the excited atomic state before spectral emission can take place. (3) Some emitted energy is absorbed by the flame. (4) The mechanism of attaining the excited species is dependent on the solvent used[1].

WAVE MECHANICS

It has been shown elsewhere[1] that the intensity of a spectral line is governed by the equations

$$S = \frac{N_2 E}{\tau} = \frac{N_1 E}{\tau} \frac{g_1}{g_2} e^{-E/kT}$$

and

$$\log Q = \frac{-5040\,V}{T}$$

where S = Strength of spectral line for the transition from excited to lower energy state
N_2 = No. of atoms in excited state
N_1 = No. of atoms in lower energy state
Q = $(N_2/N_1) \cdot (g_2/g_1)$
E = Energy difference between excited and lower energy state

V $= E$ expressed in electron volts
$g_1/g_2 =$ Statistical weights or a priori probabilities
k $=$ Boltzman's constant
T $=$ Temperature
τ $=$ Life time of excited atoms

Eqn. (1) shows very clearly the relation between the temperature, T, of a system and the intensity of spectra, S, emitted from that system. It also shows that there is a relationship between the intensity S and the energy E associated with the particular spectral line being examined. Since

$$E = h\nu \qquad (3)$$

where $h =$ Planks constant
$\nu =$ Wave number $= 1/\lambda$
$\lambda =$ Wavelength of emitted spectral line

it follows that S is a function of λ for a given temperature. Providing the ratio g_1/g_2 does not vary significantly, and if N_2 is small compared to N_1 we would expect a relationship between the observed S and λ, and hence N_2/N_1 and λ to be as shown in Fig. 1.

Fig. 1 shows the mathematical ratio of excited atoms to unexcited atoms. It is very dependent on the energy difference, E, between N_2 and N_1 and hence λ for a constant temperature. It indicates that at this temperature (3000°K) we would expect to find, in general, that emission lines with wavelength 6000 Å would be 10^7 times as intense as emission lines at 2000 Å. At higher temperatures, of course, this difference would decrease, but would still remain orders of magnitude higher.

An examination of the M.I.T. tables of intensities of spectral lines[2] shows that although there is some tendency for this relationship to be true, the intensities are much nearer to being equal than would be indicated by the mathematical relationship. This is illustrated in Table I. The lines chosen were the strongest in their wavelength range.

We would expect from eqns. (1), (2) and (3) that under standardized conditions there would be a general tendency for intensity of emission lines to increase rapidly with increase in wavelength. However, Table I illustrates that this relationship does
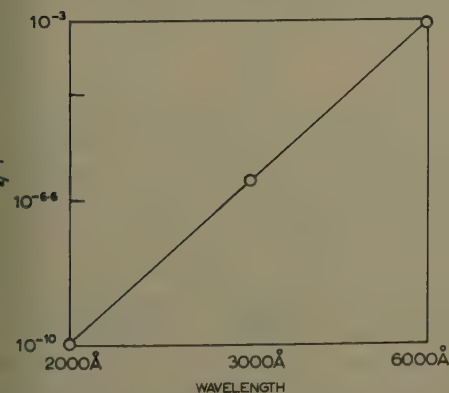

Fig. 1. Relation between N_2/N_1 and λ at a temperature of 3000°K.

TABLE I

Element	λ Å	Intensity
Sodium	5890	9000
	3302	600
Zinc	3075	150
	2138	800
Lead	4057	2000
Aluminium	3944	2000
	3082	800

not hold between the elements; neither does it hold for different spectral lines of the same element. For example, the sodium 5890 Å line should be about 10^4 as strong as the sodium 3032 Å line. Similarly, with zinc 3075 Å and 2138 Å lines. This leads to the conclusion that although the relationships shown in eqns. (1) and (2) are true in themselves, they do not tell the whole story.

It will be remembered that these equations were developed for studies of light emitted from stars where temperatures in the order of $5 \cdot 10^6 °K$ are encountered. Further, they were developed for black body conditions. At these temperatures of operation it is very probable that any other source of energy would be relatively unimportant. However, under laboratory conditions operating temperatures are much lower. Also, under laboratory conditions other sources of energy may play an important part. Ambient ultraviolet light is such an energy source. It happens that most sources for spectral excitation are also sources of U.V. light, e.g., spectrographic arc and spark, flame photometers, etc.

The relationship between absorption and wavelength is given by the equation

$$I = I_0 e^{-K_\nu C l}$$

$$\int K_\nu \mathrm{d}\nu = \frac{\pi e^2}{mc} N_\nu f$$

where I_0 = Intensity of transmitted light
   I_1 = Intensity of transmitted light after absorption
   K_ν = Absorption coefficient at wavenumber ν
   C = Concentration
   l = Path length
   N_ν = Number of atoms which can absorb at wavenumber ν
   f = Oscillator strength
   m = Mass of the electron
   c = Speed of light

As can be seen, the controlling variables are N_ν and f. The present work has been restricted to flame sources, but the conclusions should apply to spectrographic emission.

<div align="center">EXPERIMENTAL</div>

It was considered that a flame offered advantages over other sources because temperature and the spectral character could be varied independently. This allowed a study to be made of the effect of U.V. light at constant temperatures.

The flame as a source of ultraviolet light

Two types of flames were studied: (a) oxy–hydrogen, and (b) oxy–cyanogen. It was found by scanning the U.V. emission spectra of these flames that the intensity of emission could be changed considerably by changing the ratio of fuel to oxygen. It was further observed that the intensity of emission of iron spectral lines excited in these flames increased with increased U.V. light in the flame although the flame was below the maximum temperature in these cases. The results are summarized in Table I.

Results indicated increased metal emission with increased U.V. intensity in the flame but not with increased temperature. It should be noted that increased U.V. emission occurred with excess oxygen in the hydrogen flame and excess cyanogen in the second case.

Further evidence for this postulation was obtained when it was observed with the

TABLE II

ELATION BETWEEN INTENSITY OF EMISSION AND FLAME TEMPERATURE AND U.V. INTENSITY

	Oxy–Hydrogen			Oxy–Cyanogen		
	Excess H_2	Stoichio-metric (hottest)	Excess O_2	Excess $(CN)_2$	Stoichio-metric (hottest)	Excess O_2
emperature	low	medium	low	medium	high	medium
.V. emission	medium	medium	high	high	low	low
060 Å water band)
e emission	medium	medium	high	high	low	low
440 Å doublet)

xy–hydrogen flame that spectral lines with wavelengths significantly below 3000 Å ere not usually detected although many metals have intense spectrographic lines n this region, *e.g.*, lead 2393 Å, platinum 2165 Å, 2830 Å. It was noted that intense ame emission occurred at 3060 Å (OH-bands) and that metal emission lines with onger wavelengths were usually observed.

If it is conceded that the metals are excited by U.V. light, it is logical that the ntense flame radiation at 3060 Å is the shortest wavelength excitation source. Wave nechanics tells us that this radiation may excite lines of longer wavelength, but not horter wavelength. This fits in closely with experimental observation.

The results obtained with oxy–hydrogen flames are illustrated in Fig. 2. They show hat using a mol ratio 1:1 of oxygen and hydrogen, the OH-bands are more intense lthough the flame temperature is lower and the temperature of the stoichiometric :2 ratio ($O_2:H_2$) flame. This increase in sensitivity of OH-bands coincided with an ncrease in intensity of the iron lines emitted when an iron solution is aspirated into nese flames.

More supporting evidence was found when a similar study was made using an
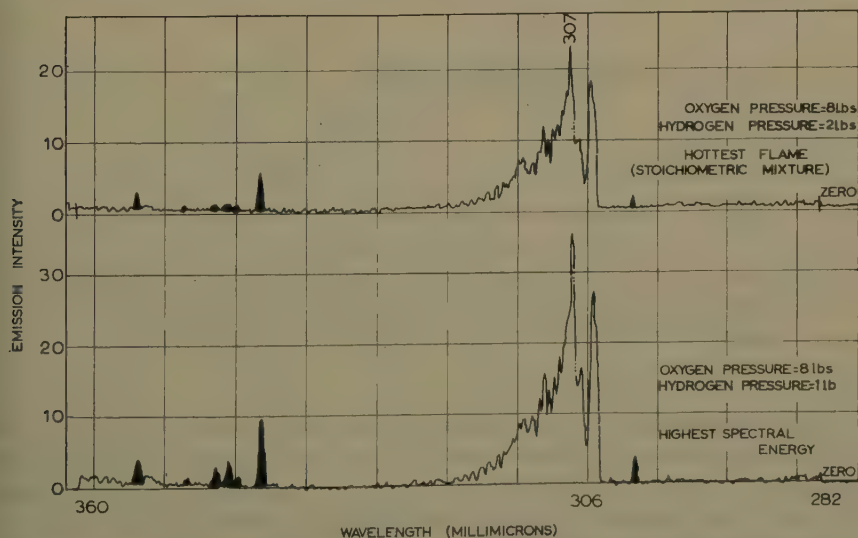
ig. 2. Spectra of iron in oxy–hydrogen flames. Iron lines (blacked in) superimposed on oxy–hydrogen flame spectrum.

oxy–cyanogen flame. The results are shown in Fig. 3. This shows the spectra betwee⟨n⟩
2300 Å and 3000 Å exhibited by oxy–cyanogen flames set at the same temperature⟨.⟩
In one flame there was excess oxygen. Very little, if any, U.V. radiation was detecte⟨d.⟩
When iron was atomized into this flame, no spectral lines were observed in this regio⟨n.⟩
The second flame contained excess cyanogen. Since these two flames were at equa⟨l⟩
temperatures, spectral variation could not be caused by temperature differences. How⟨-⟩
ever, this flame exhibited strong U.V. emission in the range 2300–3000 Å. When iro⟨n⟩
was atomized into this flame, numerous spectral lines were exhibited as can be see⟨n.⟩

These two flames differ only in their spectral character, their temperatures bein⟨g⟩
equal. It seems likely, therefore, that the difference in excitation of iron spectru⟨m⟩
is caused by the difference in U.V. light in the flame.

To summarize, if temperature were the only source of excitation, then all spectr⟨a⟩
lines, even down to 2000 Å would be excited in a flame. However, we have seen tha⟨t⟩
normally only lines with wavelengths greater than 2800 Å are excited. This coincid⟨es⟩
with the wavelength of the intense lines found in oxy–hydrogen and oxy–cyanoge⟨n⟩
flames. Further, when the oxy–cyanogen flame is distorted to radiate short wave⟨-⟩
length U.V. light, then metal emission lines are detected throughout the wavelengt⟨h⟩
band 2000 Å to 3000 Å.
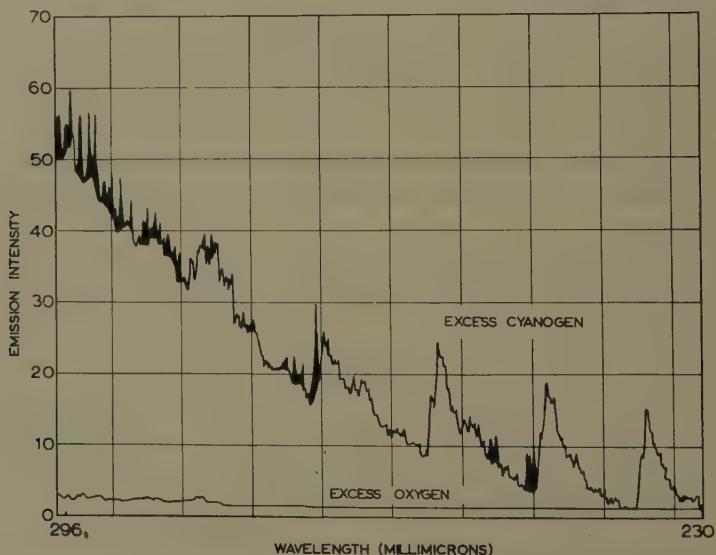
Fig. 3. Spectrum of iron in oxy–cyanogen flame. Iron lines (blacked in) superimposed on oxy⟨–⟩
cyanogen flame spectrum. Note: Cyanogen flame with excess oxygen generates no U.V. light ⟨—⟩
iron spectrum although the temperature of both flames was equal.

Measurement of flame temperature

The most widely used method of measuring flame temperatures are the line revers⟨al⟩
technique[3], and vibrational band intensity technique. However, these procedur⟨e⟩
are accurate to about $\pm 20°$. Further, it requires experience and skill to obta⟨in⟩
reliable results and, of course, difficulty would be expected in calibrating at 500⟨0°⟩
a temperature range not normally used. It was decided, therefore, to use an alterna⟨te⟩
technique. A diagram of the equipment is shown in Fig. 4.

The thermistor was sensitive to very small changes in temperature. Also, it has a small heat capacity, ensuring a short response time to come to equilibrium. Assuming the intensity of radiant energy from a flame is proportional to its temperature, it should be possible to measure the *relative* temperature of the flame. Of course, it was necessary to maintain a constant distance between the edge of the flame and the thermistor.
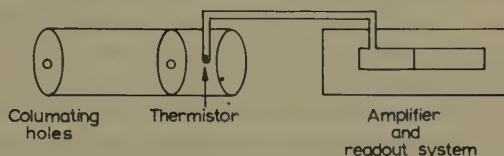

Columating   Thermistor   Amplifier
holes   and
                                          readout system

Fig. 4. Diagram of instrument for comparing flame temperature.

One advantage of this instrument is that the temperature of a small part of the flame is taken. This made it possible for a profile of the flame temperature to be obtained, and enable the maximum flame temperature to be used for comparative purposes, rather than the average flame temperature which is obtained with other techniques.

In practice it was found that a base line drift occurred caused by heating of the instrument because it was in close proximity to the flame. This problem was overcome by alternately inserting and removing a shield between the flame and the inlet of the columator and measuring the deflection obtained in the readout. This deflection is proportional to the change in temperature of the thermistor on exposure to the flame, and is therefore a function of the flame temperature. For this work, absolute flame temperatures were not measured since it was only necessary to ensure that the non-stoichiometric flames were equal in temperature.

Emission   Detector
Flame   and
atomizer   Grating   readout

Modified   Perkin-Elmer
model 13   spectrophotometer

Hollow cathode
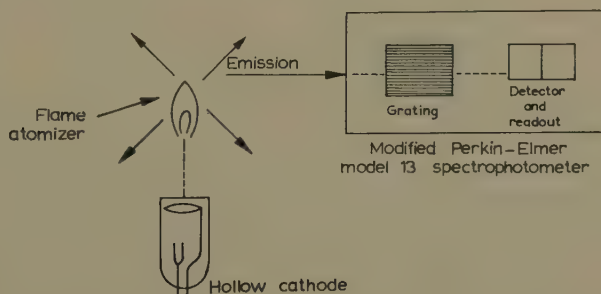
Fig. 5. Equipment used for external excitation of metal spectra.

Excitation using an external source of U.V. light

If, as has been postulated, spectra can be generated by U.V. light, it should be possible to use an external source of U.V. light to generate spectra. This was examined experimentally in the following manner.

Equipment: A schematic diagram of the equipment is shown in Fig. 5.

An aqueous solution of a suitable metal was aspirated into a standard Beckman flame photometer burner. The spectrophotometer was arranged such that the de-

tector continuously monitored the resonance line of the metal being examined. A
hollow cathode was positioned at right angles to the light path of the flame and the
slit of the spectrophotometer. The intensity of the emission was measured (a) with the
hollow cathode on and (b) with it off. If excitation of the metal atoms in the flame
occurs, there should be enhancement of the strength of the spectral line. Of course, it will
be appreciated that the metal atoms will absorb the U.V. light and re-emit at random
forming a solid sphere of radiant energy. The slit sees a very small part of this solid
angle and therefore only a very small portion of the re-emitted light would be utilized.
To detect this small amount of energy, the instrument was run at maximum sensitivity.
The results obtained were as follows:

Sodium. λ 5890 Å. No enhancement of intensity was detected. However, it was
noted that the intensity of the flame emission signal was so high that it would be
very difficult to detect the small enhancement expected.

Nickel. λ 3524.5 Å, 3414 Å. No enhancement was detected. In this case the oscil-
lator strength of these spectral lines is low. This would mean that the nickel would
be very inefficient in absorbing energy from the hollow cathode. As a result, only
a small amount of energy would be re-emitted.

Magnesium. λ 2852 Å. The results obtained with magnesium are shown in Fig. 6.

The Mg 2852 Å line gave good conditions for detection of 'fluoresced' light. The
oscillator strength of the line is high. This permits efficient absorption of energy from
the hollow cathode. Further, the original emission intensity is low, allowing the
instrument to be set at high sensitivity. Under these conditions, any re-emitted signal
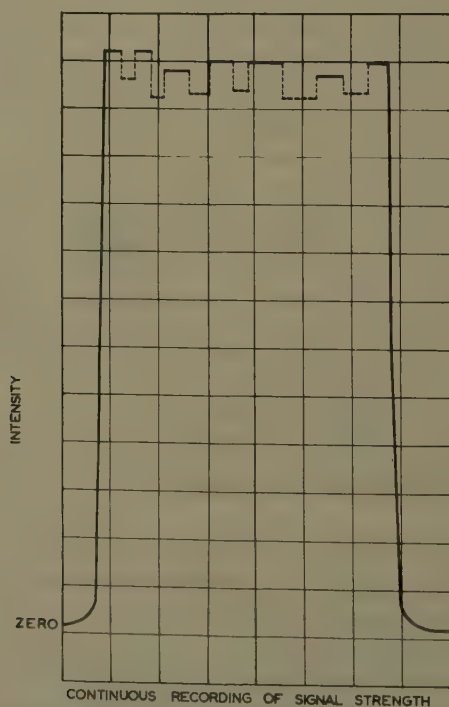
Fig. 6. Enhancement of Mg 2852 Å line using a hollow cathode. ———— Mg (1000 p.p.m.) with
hollow cathode; – – – – Mg (1000 p.p.m.) without hollow cathode.

was significant compared to the emission of the metal excited by the flame alone. This allowed a significant measurement of 'fluoresced' light to be made.

It appears from Fig. 6 that some enhancement of the signal occurred. Care was taken to prevent reflected light from the hollow cathode reaching the extrance slit of the monochromator. Further, since there was no enhancement detected in the case of sodium and nickel, it can be assumed that the reflection from the flame, or droplets in the flame, was negligible since such reflections would have caused an apparent signal in the case of these two metals.

Attempts to use a continuous source of radiation (hydrogen lamp) to cause "fluorescence" were unsuccessful. Although the total quantity of energy was much greater than that in the flame, the quantity of energy from the lamp having the correct wavelength was small. Atomic absorption indicates that absorption lines are of the order of 0.03 Å wide. This indicates that the source must not only be of sufficient energy to excite the metal atoms, but must be of the correct wavelength. A hollow cathode is a much better source of such radiation since the wavelength and intensity requirements are met more favorably. It is also important to remember that with external excitation, the atom is subjected to radiant energy coming from one direction only. However, in the environment of a flame, that atom is at the center of a sphere of radiation from the flame. Further, this radiant energy is in very close proximity compared to an external source. It can be seen, therefore, that the intensity of U.V. light in the flame is considerable greater than would be suspected from a simple measurement of its emission intensity at the wavelength considered because (a) the atom is at the center of a sphere of radiant energy, (b) the energy source is infinitely close to the atom. Both these advantages are lost with an external source.

RESULTS

The results indicated strong evidence that ambient U.V. light contributed to the intensity of the metal spectra emitted from flames. Further, it seems reasonable to conclude that we can project these results to emission spectrography.

It is well known that the strength of a metal emission line obtained from a spectrograph is modified by the matrix of the sample and by the interelement effects of elements other than the matrix. Of course, the matrix will control to some extent the volatility of the metal being examined, but it is also possible that U.V. emission from the matrix will further excite this metal if the wavelength relationship is suitable. On the other hand, of course, it is possible that the matrix absorbs light emitted by the sample metal. This would result in considerable loss of intensity of emission, depending on the ratio of metal to matrix. In conventional spectrography, great pains are taken to keep this ratio constant by laying down the sample on a standard matrix.

The same modifications of spectral intensity may also be produced by other elements present in the sample, i.e., enhancement by excitation, depression by absorption. Normally, this interelement effect is hard to control because the elements in question are often impurities in the matrix, or the sample, and only extensive purification procedures eliminate the difficulty.

Although this suggestion does not solve the problem of imprecision in spectrography, it does help to understand them, and this understanding may lead to a solution at a later date.

SECONDARY EFFECT OF U.V. LIGHT

As described elsewhere[1], it is probable that a metal becomes a hydrate and/or a oxide before breaking down to the atomic state. This process is important in contro ling the number of excited atoms produced in a flame, and hence the intensity emission. Metal hydrates and oxides usually exhibit broad band spectra and cor versely it may be expected that they would absorb energy over a similar broad wave length band. If intense U.V. light is present in the source at these wavelengths, it probable that much of this energy is absorbed and that it contributes to the break down of the molecules, releasing free atoms.

This would result in an increase in the number of excited metal atoms formed and therefore in the intensity of the spectra they emit. Under these conditions th U.V. light would not be exciting the atoms directly as with the hollow cathode, bu would be increasing the efficiency of producing the emitting species. The net effe would be an increase in spectral intensity.

CONCLUSIONS

It is concluded from these observations that the intensity of a metal emission spectrum is dependent on the following variables:

1. Flame temperature. The equations listed above indicate the temperature/emissio intensity relationship.

2. U.V. light generated in the flame. Both the wavelength and intensity of this ligh are important in exciting atoms.

3. Mechanism of producing atoms. This controls the number of ions or molecul which will be reduced to atoms by passage through a flame. Solvent and U.V. ligh affect the efficiency of this step.

4. Absorption of U.V. light by solvents or fragments of solvents present in the flam This would result in a depression of line intensity.

ACKNOWLEDGEMENT

SUMMARY

It is generally believed that emission spectra result from thermal excitation. It is proposed tha ultraviolet light present in a flame is also responsible for exciting metal atoms present. Exper mentally it has been shown that the intensity of metal emission spectra is a function of the U.\ characteristics of the flame even at constant flame temperature. It was also demonstrated tha spectral intensity can be enhanced by external radiation of U.V. light of the correct wavelengt

RÉSUMÉ

L'auteur a étudié le mécanisme de l'excitation spectrale en photométrie de flamme, montrant qu les spectres d'émission ne sont pas dus seulement à une excitation thermique, mais aussi aux r diations ultra-violettes.

ZUSAMMENFASSUNG

Es wird nachgewiesen, dass Emissions Spektren nicht allein durch thermische Anregung entstehe sondern dass die Intensität der Metall Emissionsspektren durch die ultravioletten Strahlen d Flamme stark beeinflusst wird.

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SPECTROPHOTOMETRIC STUDY OF THE BERYLLIUM–THORIN COMPLEX AND ITS APPLICATION TO THE DETERMINATION OF BERYLLIUM IN ALLOYS

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Azo dyes substituted in the *o*-position to the azo linkages combine with certain metallic ions to form characteristic closed ring compounds and these dyes can be made specific for a particular group of metals by having a functional group in the *o*-position which reacts preferentially with this group of metals[1].

In the investigation of such a compound, 1-(*o*-arsonophenylazo)-2-naphthol-3,6-disulfonic acid (thorin), for the determination of thorium, BYRD AND BANKS[2] reported that beryllium causes interference if the ratio of $BeO:ThO_2$ is 2000:1. ADAMOVITCH AND YUTSIS[3] have utilised the reaction of beryllium with thorin for the determination of beryllium in ferrous alloys.

The present paper deals with the nature and the optimum conditions for the formation of the beryllium complex with thorin and its application to the determination of beryllium in different beryllium alloys.

EXPERIMENTAL

All absorption measurements were made on a Beckman DU spectrophotometer using 1-cm pyrex cells.

Reagents

Standard beryllium chloride solution. This was prepared from pure BeO (Merck) and standardised. Aliquots of the stock solution were diluted to give $2 \cdot 10^{-4}$ *M* Be solutions.

Thorin solution. Thorin supplied by Eastman Kodak (White Label) was purified by recrystallization. The purity was determined by potentiometric titration[4] and was found to be 98% (Fig. 1). This purified reagent was used throughout the work.

Optimum pH and wavelength

Aliquots containing 10 μg of beryllium were treated with excess thorin in 25-ml volumetric flasks, the pH of the solutions being varied from 1 to 13. The absorption spectra of these solutions measured against reagent blanks showed maximum absorbance at pH 12 and at 470 mμ.

Beryllium–thorin complex

The formula of the complex was determined by various methods.

(a) *Job's method of continuous variation*[5,6]. The spectra of solutions with the ratios of reagent to metal 1:1, 2:1 and 3:1 were measured against reagent blanks. No iso-bestic points were observed, thus the formation of a single complex with maximum absorbance at 470 mμ at pH 12 was indicated. Fig. 2 indicates the results obtained at 470 and 530 mμ, the pH being adjusted to 12 by borate–sodium hydroxide buffer. Only a 1:1 complex is indicated.
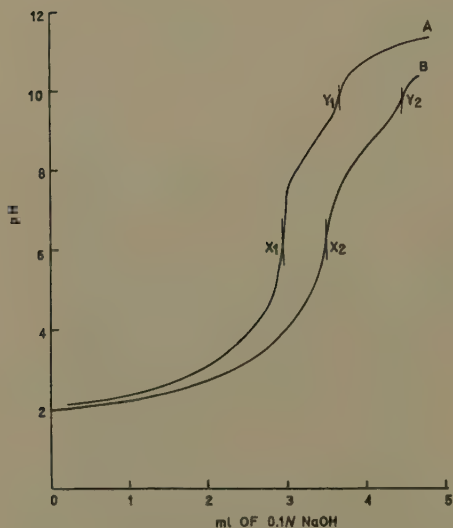

Fig. 1. Potentiometric titration of 10 ml 0.01 *M* Thorin. A: before purification; B: after purification. $x_1, y_1 = 0.75$ mequiv., A = 75% pure; $x_2, y_2 = 0.98$ mequiv., B = 98% pure.
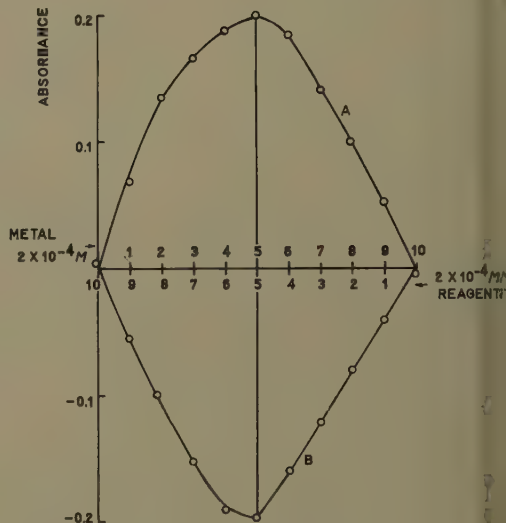
Fig. 2. Continuous variation. A: at 470 mμ; B: at 530 mμ.
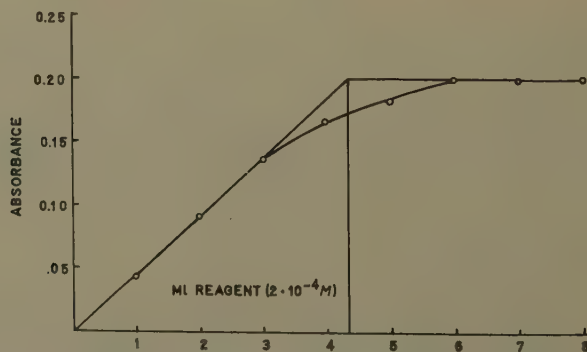
Fig. 3. Mole ratio method. Metal ion concentration 4 ml of 2·10^{-4} *M*

(b) *Mole ratio method*[7]. The results obtained (Fig. 3) indicate the formation of a 1:1 complex. The measurements were made at 470 mμ and at pH 12.

(c) *Slope ratio method*[8]. The composition of the complex was also checked by the slope ratio method. Measurements were made at 470 mμ for solutions adjusted to pH 12 with sodium hydroxide–borate buffer. A 1:1 complex was clearly indicated (Fig. 4). All the methods show that 1:1 complex is formed between beryllium and thorin.
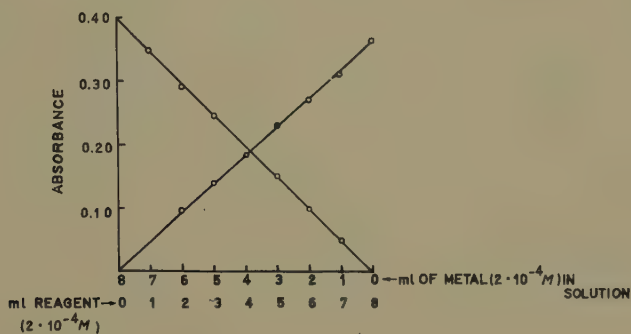
Fig. 4. Slope ratio method.
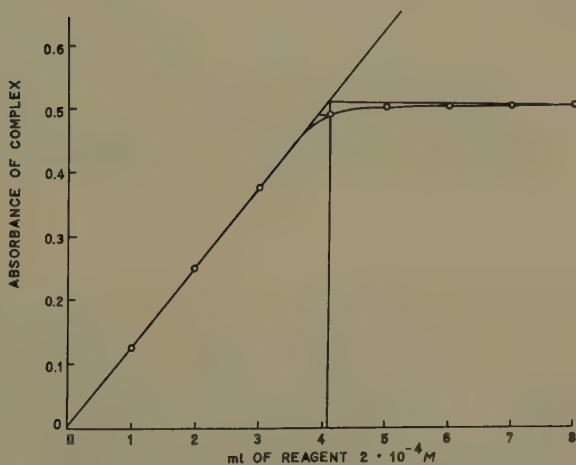
Fig. 5. Approximate dissociation constant.

Dissociation constant

By the method of STEARNS[9] the approximate dissociation constant of the complex was calculated. Aliquots of 4 ml of $2 \cdot 10^{-4}$ M thorin were placed in 25-ml flasks and $2 \cdot 10^{-4}$ M beryllium solution was added in amounts varying from 0 to 8 ml (2 equivalents). The solutions were diluted to 25 ml with buffer of pH 12, and the absorbancies were measured at 470 mμ (Fig. 5). An approximate value of the dissociation constant was calculated from the above data. From this value the amount of free reagent formed by dissociation and hence its absorbance was calculated. This was subtracted

from the total absorbance to give the absorbance due to the complex and the dissoc
ciation constant was again calculated. Similar successive approximations were made
till a constant value for the dissociation constant, $1.38 \cdot 10^{-7}$, was obtained.

Determination of beryllium in alloys

Beryllium alloyed with other metals like Cu, Ni, Fe, Zn, Al etc., confers certain
desirable properties on these alloys. The percentage of beryllium usually varies from
0.05% to 2.0%. Thorin cannot, however, be used directly for the determination of
beryllium in these alloys since metals like Ca, Mg, Fe, etc., interfere. Acetylacetone
forms well-defined chelates with a number of metals including beryllium. Many of
these chelates are highly soluble in organic solvents so that macro and micro separa-
tions are feasible[10]. If EDTA is used as masking agent a basis is found for the sepa-
ration of beryllium as acetylacetonate from other metals like Fe, Al, Zn, Cu, Cr
etc.[10]. The procedure thus evolved for the separation of beryllium before its determi-
nation is described below.

Standard beryllium solutions of strength 1 ml = 100 μg and 1 ml = 10 μg were
prepared from the stock solution.

Standard curve

Standard beryllium solutions containing 1–10 μg of beryllium were placed in 25-ml
volumetric flasks and 2 ml of aqueous 0.1% thorin solution was added. The solutions
were diluted to 25 ml with sodium hydroxide–borate buffer to give a final pH of 12.
The optical densities of the solutions were measured at 470 mμ against a reagent blank
on a Beckman DU spectrophotometer using 1-cm pyrex cells. Standards were also
taken for the 20–100 μg range of beryllium using 10 ml of 0.1% thorin, the final
volume in this case being 100 ml. The results show that Beer's law is obeyed in both
cases.

Procedure for samples

To about 10 ml of solution containing 1–100 μg of beryllium, 5 ml of aqueous 10%
EDTA was added. The pH was adjusted to 4–5 by the addition of dilute ammonia
using pH indicator paper. One ml of aqueous 15% (v/v) acetylacetone was added
followed by two drops of concentrated ammonia to bring the pH between 7 and
as seen by pH indicator paper. The solution was allowed to stand for 5 min and then
shaken with 5 ml of carbon tetrachloride for 7 min. The organic layer was transferred
to another clean separating funnel. The extraction was repeated thrice with fresh 5-ml
portions of carbon tetrachloride after adding 1.0 ml of acetylacetone each time.

The combined organic layers were shaken for 7 min with 3 ml of concentrated
hydrochloric acid diluted to 7 ml with water and the organic phase was then rejected.
The aqueous phase was evaporated to dryness and fumed with perchloric acid. The
residue was taken up in a little water, thorin added and the pH adjusted to 12 using
borate–sodium hydroxide buffer. The absorbance was measured at 470 mμ against
a reagent blank.

Table I shows the optical densities obtained with thorin for beryllium solution
(1) taken through the procedure and (2) by direct development of colour; these agree
well.

TABLE I

Be in μg	Optical density with thorin				
	Directly			Through procedure	
per 25 ml					
1	0.029	0.028	0.029	0.029	0.030
2	0.055	0.059	0.059	0.058	0.060
3	0.085	0.090	0.085	0.082	0.087
4	0.112	0.110	0.115	0.110	0.114
5	0.144	0.140	0.145	0.143	0.145
6	0.177	0.175		0.171	0.175
8	0.230	0.235		0.230	0.232
10	0.295	0.300		0.290	0.295
per 100 ml					
25	0.180	0.177		0.178	0.185
50	0.355	0.365		0.355	0.360
75	0.530	0.520		0.525	0.515
100	0.720	0.710		0.712	0.730

Determination of beryllium in Cu–Be alloys

0.1072 g of the alloy was dissolved in dilute nitric acid, evaporated to dryness and diluted to 250 ml with distilled water. A 10-ml aliquot was transferred to a separating funnel and beryllium was separated by the above procedure. The colour was developed with 10 ml of 0.1% thorin in a final volume of 100 ml at pH 12 and its absorbance was measured against a reagent blank at 470 mμ. In order to see whether the recovery of beryllium was quantitative, a standard beryllium solution was added to another 10-ml aliquot and beryllium estimated. The results are shown in Table II. The percentage of Be in the sample was also checked by a gravimetric procedure[11] and was found to be 1.93; this is in good agreement with the values obtained by the present method.

TABLE II

Amount of Cu–Be alloy taken in mg	Amount of Be added in μg	Amount of Be found in μg	% Be
4.288	Nil	79.31	1.85
4.288	Nil	80.00	1.86
4.288	Nil	77.90	1.82
4.288	10	88.7	
4.288	10	89.6	

Determination of beryllium in other alloys

Beryllium is also a constituent of ferrous and non-ferrous alloys. The compositions of these alloys are given in Table III. Synthetic alloy solutions were prepared by taking beryllium and other metals in the respective proportions as nitrates. As chlorides, nitrates or sulphates do not interfere with the extraction of beryllium as acetylacetonate, any of these acids can be utilised for the dissolution of the alloy. Aliquots containing 10 mg of the alloys were taken and beryllium was determined as described above.

Determination of beryllium in steel

Recoveries were also carried out after addition of a known amount of beryllium to a stainless steel solution. 0.1 g of a high speed steel (British Chemical Standard

TABLE III

Description of alloy	Composition of synthetic alloy mixture	Beryllium found %		
Be–Cu alloy	0.5% Be 1.5% Co 0.7% Ni 1.0% Ag 96.3% Cu	0.483 0.482 0.475 Mean: 0.48		
Ferrous alloy[a]	0.05% Be 15.00% Ni 20.00% Cr 7.00% Mo 32.00% Co 8.00% W 2.00% Mn 15.95% Fe	0.049 0.046	0.048	0.048
		Mean: 0.048		
Ferrous alloy[b]	0.8% Be 50.0% Ni 49.2% Fe	0.75 0.77 0.75 Mean: 0.76		
Zinc base alloy	0.1% Be 2.2% Cu 97.7% Zn	0.097 0.098 0.10 Mean: 0.098		
Light alloy	0.2% Be 5.0% Mg 1.0% Si 0.3% Mn 0.15% Ti 93.35% Al	0.18 0.18 0.20 Mean: 0.19		

[a] In the case of the alloy containing tungsten, tungstic acid is precipitated when the alloy treated with acid, but on addition of EDTA and then NH_4OH, it goes into solution as ammonium tungstate at pH 6–7. An aliquot of this solution was taken and after addition of 1 ml of acetyl acetone, beryllium was estimated in the usual way.
[b] For the alloy containing a high percentage of iron, it is necessary to repeat the extraction of beryllium as acetylacetonate from the first acid extract to ensure complete removal of iron.

No. 241) of the composition given in Table IV was dissolved in 2 ml of 1:1 hydrochloric acid and the carbon was oxidised by the addition of a few drops of nitric acid. solution equivalent to 50 μg of beryllium was then added followed by 50 ml of 10 EDTA and then ammonia (1:1) till the solution became clear. It was then diluted to 100 ml. 10 ml of the solution was pipetted out into a separating funnel and 1 m of acetylacetone was added. The pH was brought to 7–8 by addition of dilute am monia and extractions were carried out with carbon tetrachloride. After the beryllium had been extracted into acid, the acetylacetonate extractions were repeated to ensu complete removal of iron. The results (Table IV) show that the method can be applie to the determination of beryllium in its alloys.

TABLE IV

Composition of sample BCS No. 241 (High speed steel)	Total Be added in μg	Be found in μg	Recovery %
W = 6.74%			
Mo = 4.17%			
Cr = 4.61%			
V = 1.35%	50	47	94
Co = 0.67%			
C = 0.86%			
Si = 0.30%			
S = 0.039%			
P = 0.024%	50	48	96
Mn = 0.25%			
Ni = 0.15%			
Cu = 0.14%			
Sn = 0.04%			

SUMMARY

A spectrophotometric study of the beryllium complex with purified thorin shows the formation of a 1 : 1 complex at pH 12. The dissociation constant obtained after successive corrections for reagent absorbance is $1.38 \cdot 10^{-7}$. Beryllium in concentrations of 0.05% to 2.0% in copper base, zinc base, aluminium base and ferrous alloys can be determined by the formation of the thorin complex after its preliminary separation as acetylacetonate in presence of EDTA.

RÉSUMÉ

Les auteurs ont effectué une étude spectrophotométrique sur le complexe béryllium–thorin. Des méthodes sont décrites pour le dosage du béryllium dans ses alliages.

ZUSAMMENFASSUNG

Beschreibung einer spektrophotometrischen Bestimmung von Beryllium in seinen Legierungen mit Hilfe von Thorin.

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SPEKTROPHOTOMETRISCHE BESTIMMUNG VON NIOB MIT ASCORBINSÄURE

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Ascorbinsäure wurde schon früher von HINES UND BOLTZ[1] sowie KORKISCH UN[ ]
FARAG[2] zur spektrophotometrischen Bestimmung von Titan, mit dem sie einen gelbe[ ]
Komplex bildet, verwendet. Sie bildet auch mit Niob eine gelbgefärbte Verbindung[ ]
die in demselben Wellenlängenbereich wie der Titanascorbinatkomplex maxima[ ]
Extinktion aufweist. Da das Beersche Gesetz über einen weiten Konzentrationsbereic[ ]
gilt und die Handhabung der Methode relativ leicht ist, weist die hier beschrieben[ ]
gegenüber den üblichen Methoden zur photometrischen Bestimmung des Niobs[3] nich[ ]
zu unterschätzende Vorteile auf.

LÖSUNGEN UND REAGENTIEN

Niob- und Tantalstandardlösungen

0.1969 g Nb_2O_5 wurden zusammen mit 5 g wasserfreiem Kaliumcarbonat eine halb[ ]
Stunde lang in einem Platintiegel geschmolzen, die Schmelze abkühlen gelassen un[ ]
schliesslich in insgesamt 100 ml Wasser gelöst. Diese carbonat-alkalische Nioba[ ]
lösung enthielt 1 mg Nb/ml. Auf analoge Weise wurde eine Tantalatlösung durc[ ]
Schmelzen von 0.1222 g Ta_2O_5 hergestellt, die 1 mg Ta/ml enthielt. Durch entspr[ ]
chendes Verdünnen mit dest. Wasser wurden aus diesen Stammlösungen Lösunge[ ]
mit geringeren Niob- bezw. Tantalgehalten hergestellt.

Ascorbinsäurelösung

Unter Verwendung von reiner Ascorbinsäure der Wiener Heilmittelwerke wurd[ ]
eine 10%-ige Lösung dieser Säure in dest. Wasser hergestellt. Diese Lösung mu[ ]
allerdings immer unmittelbar vor ihrer Verwendung frisch bereitet werden und i[ ]
vielen Fällen ist die Verwendung fester Ascorbinsäure vorzuziehen.

Ferner wurden angewendet

Standardlösungen einer Anzahl von Fremdionen (s. Tab. II), 4 N und 1 N Salzsäur[ ]
2.5 M Natriumacetatlösung sowie wasserfreies Kaliumcarbonat *p.a.*

APPARATE

Die photometrischen Messungen wurden mit einem Beckmann Spektrophotomete[ ]
Modell B, bei einer Wellenlänge von 345 mμ in 1-cm Küvetten ausgeführt.

ABHÄNGIGKEIT DER EXTINKTION VON DER WELLENLÄNGE

ml einer Niobatlösung, die 200 μg Nb/ml enthielt, wurde mit 5 ml 10%-iger Ascorbin-
säure, 1 ml 2.5 M Natriumacetatlösung und 0.6 ml 1 N Salzsäure in einem 10-ml
Messkolben mit dest. Wasser zur Marke aufgefüllt und die Extinktion dieser Lösung
im Wellenlängenbereich von 310 bis 410 mμ gegenüber einer analog hergestellten
Reagensleerlösung gemessen. Die Ergebnisse dieser Messungen sind aus Tabelle I
ersichtlich. Daraus ist zu entnehmen (Spalte 2) dass das Maximum der Extinktion
bei einer Wellenlänge von 345 mμ liegt.

TABELLE I

Wellenlänge in mμ	Extinktion von Niob	Extinktion von Tantal
310	0.065	0.015
320	0.220	0.140
325	0.330	0.190
330	0.385	0.200
335	0.400	0.185
340	0.415	0.160
345	0.420	0.145
350	0.410	0.120
360	0.385	0.085
370	0.340	0.060
380	0.310	0.040
390	0.280	0.030
400	0.230	0.020
410	0.145	0.010

Analoge, in einem 50-ml Messkolben durchgeführte, Messungen bei denen 1 mg
Niob, 25 ml 10%-ige Ascorbinsäure, 5 ml 2.5 M Natriumacetatlösung und die zur
Neutralisation der carbonatalkalischen Lösung erforderliche Menge an verdünnter
Salzsäure (*vide infra*) angewendet wurden, ergaben Resultate, die mit den in Spalte 2
angegebenen identisch waren.

In Spalte 3 der Tabelle I sind die Ergebnisse der unter völlig gleichen Bedingungen
mit Tantal ausgeführten Messungen wiedergegeben. Daraus geht hervor, dass das
Maximum der Tantalextinktion bei 330 mμ liegt.

EINFLUSS DER SALZSÄUREKONZENTRATION

Die optimale Salzsäuremenge variiert natürlich mit dem Carbonatgehalt der Stamm-
lösung. Beim Arbeiten in 10-ml Messkolben nach Aufschluss einer Niobpentoxyd-
menge von 0.1969 g mit 5 g Kaliumcarbonat wurde bei einem konstanten Gehalt
von 3 ml 10%-iger Ascorbinsäurelösung, 1 ml 2.5 M Natriumacetatlösung und einem
aliquoten Teil der verdünnten Niobatlösung, der 200 μg Niob enthielt, die in Fig. 1
gezeigte Kurve erhalten. Da bei Anwendung von 0.3 bis 1.0 ml 1 N Salzsäure prak-
tisch immer dieselbe Extinktion erzielt wurde, wird demnach im Weiteren nur mehr
das in der Mitte des Konstanzbereiches liegende Volumen von 0.6 ml 1 N HCl/10 ml
Messlösung bei sonst gleichen Bedingungen verwendet und damit im Konzentrations-
bereich von 10–400 μg Niob eine lineare Abhängigkeit der Extinktion von der Kon-
zentration erhalten.

Beim Arbeiten in 50-ml Messkolben und mit wechselnden Carbonatgehalten der Niobatlösung wird die erforderliche Salzsäuremenge folgendermassen ermittelt: 10 ml der Stammlösung, die durch Ausziehen des Aufschlussgutes (0.1–1.0 g Substanz mit bis zu 10 g Kaliumcarbonat) mit 100 ml dest. Wasser erhalten wird, werden mit 1 N
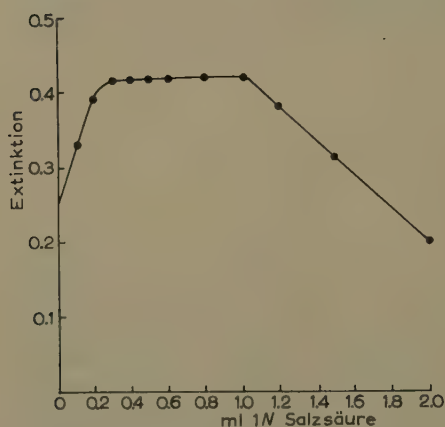

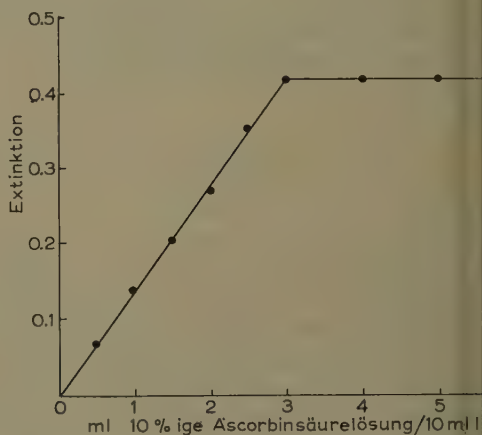Fig. 1. Einfluss der Salzsäurekonzentration.   Fig. 2. Einfluss der Ascorbinsäurekonzentration

Salzsäure unter Verwendung von Phenolphthalein als Indikator auf farblos titriertt Wenn a ml der 1 N Salzsäure verbraucht wurden, so muss pro ml der Stammlösung eine Menge von $x = a \cdot 0.6$ ml 4 N Salzsäure bzw. die vierfache Menge 1 N HCl/50 ml Messlösung zugesetzt werden. Es wurden Messlösungen mit Gehalten von 2.5–25 ml einer 10%-igen Kaliumcarbonatlösung und Niobgehalten von 500 und 1000 μg Nb/50 ml mit der ermittelten Salzsäuremenge versetzt und die so erhaltenen Ergebnisse stimmten innerhalb von $\pm$ 4.0% überein.

EINFLUSS DER ASCORBINSÄUREKONZENTRATION

Wie aus Fig. 2 hervorgeht wird die maximale Extinktion schon bei Anwesenheit von 3 ml der 10%-igen Ascorbinsäurelösung/10 ml Messlösung erreicht, doch haben wir später immer einen Überschuss und zwar 5 ml der 10%-igen Ascorbinsäurelösung bzw. 0.5 g feste Ascorbinsäure/10 ml zugesetzt, wodurch etwa vorhandene Manganat-ionen reduziert werden können, ohne dass die Ascorbinsäurekonzentration dabei praktisch abnimmt.

EINFLUSS VON TEMPERATUR UND ZEIT

Da die Anwesenheit des aus dem Carbonat in Freiheit gesetzten Kohlendioxydes in der Messlösung eine reproduzierbare Messung unmöglich machen würde, haben wir auf verschiedene Weise versucht diesen Einfluss auszuschalten. Am besten ist es, da Kohlendioxyd aus den Lösungen mit Unterdruck abzusaugen. Nach einstündigem Evakuieren im Vakuumexsikkator mit einer gut ziehenden Wasserstrahlpumpe is alles überschüssige Kohlendioxyd abgesaugt (es steigen keine Blasen mehr auf). Nach

dem Auffüllen und mehrmaligen Umschütteln wird der Messkolben mit Leitungs-
wasser auf eine Temperatur von 15 bis 20° gebracht, da die Extinktion zwischen 12
und 20° praktisch konstant ist. Oberhalb 20° fällt sie ab und geht bei Temperaturen
über 40° rasch gegen Null. Nach Ablauf von 10 min wird dann die Extinktion gemessen
und verändert sich während der nächsten 30 min um höchstens 2.0%. Hierauf beginnt
sie zuerst langsam, dann etwas schneller abzunehmen.

GÜLTIGKEIT DES BEERSCHEN GESETZES

Die Lösungen enthielten von 0 bis 50 μg Nb oder Ta/ml. Beim Arbeiten in 10-ml
Messkolben gilt das Beersche Gesetz im Konzentrationsbereich von 2–40 μg Nb/ml,
beim Arbeiten in 50-ml Kolben von 0.5 bis 40 μg/ml Messlösung. An Reagentien waren
in den 10-ml Messkolben: 0.5 g Ascorbinsäure, 1 ml der 2.5 M Natriumacetatlösung
und 0.6 ml 1 N Salzsäure sowie 0–500 μg Niob oder Tantal mit der entsprechenden
Carbonatmenge (bzw. nach der Säurezugabe Kaliumchlorid) enthalten. In den 50-ml
Messkolben waren 2.5 g Ascorbinsäure, 0–2500 μg Niob oder Tantal + Kaliumcar-
bonat, 5 ml der 2.5 M Natriumacetatlösung und die berechnete Salzsäuremenge
zugegen. Die Extinktion wurde für Niob bei 345 mμ (Kurve I) und 360 mμ (Kurve
II), für Tantal bei 330 mμ (Kurve III) und 360 mμ (Kurve IV) gemessen (s. Fig. 3).
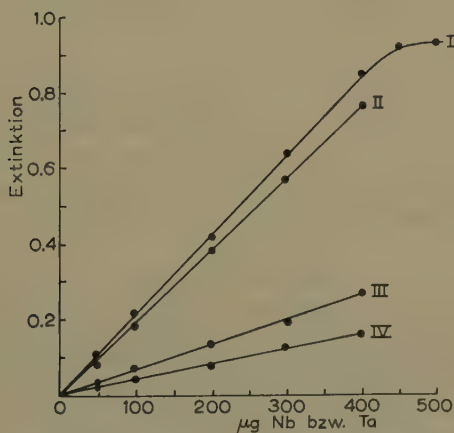
Fig. 3. Gültigkeit des Beerschen Gesetzes.

Wie aus den Kurven III und IV ersichtlich ist, lässt sich Tantal ebenfalls mit
Ascorbinsäure photometrisch bestimmen, wobei aber die Messgenauigkeit infolge der
ungenügenden Steilheit der Eichkurve relativ gering ist.

EMPFINDLICHKEIT DER METHODE UND EINFLUSS DER REAGENTIENZUGABE

2–40 μg bzw. 0.5–40 μg Nb/ml sind noch bestimmbar. Der prozentuelle Fehler beträgt
±3–4%. Die Reihenfolge der Reagentienzugabe ist ohne Einfluss, doch ist es gün-
stiger die Ascorbinsäure zuerst in den trockenen Messkolben einzuwägen.

EINFLUSS VON FREMDIONEN

In Tabelle II wird der Einfluss einer Reihe von Fremdionen gezeigt.

TABELLE II

Eingesetzte Niobmenge in μg		Gleichzeitig anwesendes Fremdion	Wiedergefundene Niobmenge in %
200	1	mg Kaliumphosphat	73.0
200	2	mg Natriumsulfat	99.0
200	0.1	g Kaliumchlorid	100.0
200	1	mg Kaliumjodid	102.5
200	1	mg Kaliumbromid	62.0
200	0.1	g Kaliumnitrat	96.0
200	1	mg Natriumfluorid	27.0
200	200	μg Ammoniumbichromat	104.0
200	200	μg Uranylchlorid	140.0
200	200	μg Aluminiumchlorid	118.0
200	200	μg Vanadium als Vanadat	169.0
200	200	μg Molybdän als Molybdat	135.0
200	200	μg Wolfram als Wolframat	110.0
200	200	μg Nickel als Chlorid	112.0
200	200	μg Cobalt als Chlorid	120.0
200	200	μg Mangan als Manganat	108.0
200	1	ml 0.1 M ÄDTA-Lösung	10.0
200	100	μg Tantal	115.0
200	200	μg Tantal + 1 ml 0.1 M ÄDTA-Lösung	0.0
200	100	μg Titan	190.0

Man sieht aus den Eichkurven I und III, dass eine Menge von 20% Tantal (bezogen auf Niob) einen Fehler von +8% verursacht. Misst man jedoch die Extinktion bei 360 mμ (Eichkurven II und IV) anstatt bei 345 mμ, so verursachen erst ca. 40% Tantal den gleichen Fehler.

ARBEITSVORSCHRIFT

(a) Für Niobgehalte von 0.5 bis 8% und darüber bei einer Einwaage von 0.5 g der Probe oder weniger nach 1/2 stündigem Aufschluss mit 5 g Kaliumcarbonat.

Das Schmelzgut wird mit insgesamt 100 ml dest. Wasser aufgenommen und dabei gleichzeitig in einen 100-ml Messkolben gebracht. 1 ml dieser, oder 1 ml einer entsprechend mit dest. H$_2$O verdünnten Lösung, die insgesamt 20–400 μg Nb/ml enthalten soll, wird in einen 10-ml Messkolben gebracht, in den vorher 0.5 g Ascorbinsäure eingewogen worden waren. Hierauf wird 1 ml der 2.5 M Natriumacetatlösung, 0.6 ml 1 N Salzsäure und etwas dest. Wasser zugesetzt, sodass der Kolben etwa halbvoll ist. Die Messlösung wird dann zusammen mit der Leerlösung, die ebenfalls 0.5 g Ascorbinsäure und 1 ml der Natriumacetatlösung aber keine Salzsäure im halbvollen Kolben enthält, in einen Vakuumexsikkator gestellt und eine Stunde lang mit einer Wasserstrahlpumpe evakuiert. Anschliessend werden die Kolben herausgenommen, mit dest. Wasser aufgefüllt, mehrmals umgeschüttelt und mit Leitungswasser auf gleiche Temperatur gebracht. Nach Ablauf von 10 min wird dann die Messung ausgeführt. Die Extinktion bleibt nahezu 30 min lang konstant.

(b) Für Gehalte von 0.01–4.0% bei einer Einwaage von 0.1–2 g Probe nach 1/2 stündigem Aufschluss mit 10 g Kaliumcarbonat.

Der erkaltete Schmelzkuchen wurde dann wie unter (a) beschrieben weiter be-

andelt. Der 100 ml betragenden Lösung werden 10 ml entnommen, auf 50 ml
verdünnt und unter Verwendung von Phenolphthalein als Indikator mit 1 N Salzsäure
kalt auf farblos titriert, wodurch ein Verbrauch von a ml erhalten wird. In ein 150-ml
Becherglas werden 2.5 g Ascorbinsäure eingewogen und mit 5 bis 25 ml der niob-
haltigen Lösung, die insgesamt 25 bis 2000 μg Niob enthalten sollen, versetzt. Hierauf
werden 5 ml der 2.5 M Natriumacetatlösung und $a \cdot 0.6$ ml 4 N bzw. $a \cdot 2.4$ ml 1 N
Salzsäure mal der Anzahl der ml an zugesetzter Probelösung zugegeben, das Becher-
glas mit einem Uhrglas bedeckt und in den Vakuumexsikkator gebracht. Eine Lösung
bestehend aus 2.5 g Ascorbinsäure, 5 ml der Natriumacetatlösung und 25 ml Wasser
wird als Leerlösung ebenfalls in einem bedecktes Becherglas in den Exsikkator gebracht.
Nach 1 stündigem Evakuieren mit der Wasserstrahlpumpe werden die Lösungen in
50-ml Messkolben transferiert, mit dest. Wasser aufgefüllt, umgeschüttelt, mit
Leitungswasser auf eine konstante Temperatur gebracht und schliesslich die Messung
ausgeführt. Die Eichkurve ist die gleiche wie für (a) (s. Fig. 3).

ZUSAMMENFASSUNG

Es wird eine Methode zur spektrophotometrischen Bestimmung von Niob unter Verwendung von
Ascorbinsäure als photometrisches Reagens beschrieben. Diese bildet mit Niob einen gelbgefärbten
Komplex der bei der Wellenlänge von 345 mμ maximale Extinktion aufweist. Das Gültigkeits-
bereich des Beerschen Gesetzes ist sehr gross, wodurch es möglich ist, sehr geringe wie auch relativ
grosse Mengen an Niob quantitativ zu erfassen.

SUMMARY

A method is described for the spectrophotometric determination of niobium, with ascorbic acid
as reagent. A yellow colour is formed with an extinction maximum at 345 mμ.

RÉSUMÉ

Une méthode est décrite pour le dosage spectrophotométrique du niobium, au moyen de l'acide
ascorbique comme réactif. Il y a formation d'une coloration jaune, avec extinction maximum à
345 mμ.

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APPLICATION DE LA CHRONO-AMPÉROMÉTRIE PAR REDISSOLUTION ANODIQUE AU DOSAGE DE TRACES D'ACÉTATE DE TRIPHÉNYL-ÉTAIN

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INTRODUCTION

Parmi les nombreux dérivés organiques de l'étain, étudiés par VAN DER KERK et ses collaborateurs[1], plusieurs ont été reconnus comme présentant des propriétés fongistatiques[2]; seul cependant, jusqu'à présent, l'acétate de triphényl-étain semble posséder des propriétés intéressantes qui le rendent propre à un usage agricole[3].

Aussi ne parait-il pas inutile de pouvoir mettre au point une méthode simple, rapide et suffisamment sensible, pour déterminer ce composé à l'état de traces sur végétaux ayant subi un traitement fongicide.

PRELIMINAIRES

Le dosage de faibles quantités d'acétate de triphényl-étain a été réalisé récemment par polarographie classique en mettant à profit la vague de réduction $Sn^{+2} \rightarrow Sn^{+4}$; la limite de sensibilité obtenue se situe à 6 μg dans 5 ml de liqueur (1.25 μg/ml).

Cette limite peut être considérablement améliorée en remplaçant l'électrode gouttante habituelle par une électrode à gouttes de mercure stationnaire (Electrode à goutte de mercure pendante) dont il existe à l'heure actuelle plusieurs types[5-8].

Outre les renseignements qu'il peut fournir sur le mécanisme des réactions électrochimiques[9], ce type d'électrode peut, dans un but analytique, servir de siège au dépôt pré-électrolytique des métaux amalgamables. A la fin du temps de pré-électrolyse choisi d'autant plus long que la concentration des ions à réduire est plus faible, le potentiel, maintenu jusqu'alors à une valeur correspondant au courant limite de diffusion, est ramené, à vitesse constante, vers les valeurs plus positives. La courbe de dissolution anodique (Désalmagamation) est enregistrée au moyen de l'appareil polarographique ordinaire.

CONDITIONS OPÉRATOIRES

Appareillage

Le polarographe utilisé est du type Polarecord E 261 de Metrohm (Hérisau-Suisse).

La cellule d'électrolyse, d'une capacité de 20 ml est thermostatisée à 25° ± 0.05°. La désoxygénation des solutions est réalisée par barbotage d'azote très pur pendant 5 min.

L'électrode à goutte pendante utilisée a été conçue par Vogel[8]; elle permet la formation aisée de gouttes de mercure reproductibles à $\pm 1\%$. La vitesse de balayage des potentiels est fixée à 333 mV/min; l'électrode de référence utilisée est du type Ag/AgCl/KCl saturé.

Les caractéristiques de la goutte étaient dans nos essais:

masse	1.32 mg	surface	4.75 mm²
volume	0.975 mm³	diamètre	1.23 mm

Les solutions n'ont pas été agitées au cours de la pré-électrolyse; l'atténuation (Damping) restait à la valeur nulle et le courant capacitif, très faible, n'était pas compensé.

Préparatifs analytiques

L'extraction de l'acétate de triphényl-étain sur matériel végétal est effectuée d'après les indications de Gorbach et Bock[4]; l'extrait chloroformique obtenu est agité dans une boule à décantation pendant 2 min avec 20 ml d'hydroxyde de potassium $N/10$ et 10 ml de tartrate dipotassique $N/2$.

Après repos, la couche chloroformique est soutirée: on rince la couche aqueuse avec 20 ml de chloroforme qu'on ajoute à la couche soutirée. On filtre les extraits chloroformiques: le filtrat, additionné de 3 ml d'acide sulfurique concentré, est évaporé au bain-marie. Le résidu d'évaporation est repris par 3 ml d'alcool et transvasé dans un vase de Berlin de 100 ml (forme haute); il y subit une minéralisation par chauffage avec le mélange habituel H_2SO_4–HNO_3 auquel, en fin d'opération, on ajoute quelques gouttes d'eau oxygénée à 100 volumes.

Le résidu minéralisé doit être incolore et exempt d'acide sulfurique qui trouble les mesures polarographiques: on chasse les dernières traces d'acide sulfurique par chauffage au four électrique à 250°.

Les produits de minéralisation sont alors dissous dans l'acide chlorhydrique 5 N; on porte à un volume connu (avec HCl 5 N) et on passe la liqueur au polarographe.

Enregistrement polarographique

La solution stannique (ou stanneuse) à analyser est introduite dans la cellule d'électrolyse et désoxygénée à l'azote très pur, pendant 5 min; puis elle est soumise à l'électrolyse sur goutte pendante de mercure à la tension de —0.7 V S.Ag.E. pendant exactement 5 min: on enregistre immédiatement le pic de dissolution anodique de l'étain entre —0.7 et —0.1 V S.Ag.E. et on se reporte à une courbe de calibrage.

Établissement de la courbe de calibrage

On prépare une solution titrée d'acétate de triphényl-étain: dans ce but, on minéralise un poids connu d'acétate de triphényl-étain dans l'acide chlorhydrique concentré; on porte à un volume connu, tel que la concentration finale en acide chlorhydrique soit 5 N. On peut encore préparer une solution titrée à partir d'étain métallique pur dissous dans l'acide chlorhydrique concentré tiède.

Dans une série de ballons jaugés de 25 ml on introduit successivement des volumes croissants de liqueur titrée en étain et on porte le volume des ballons au trait avec l'acide chlorhydrique 5 N. Après homogénéisation, on verse une partie de la solution

dans la cellule d'électrolyse en vue de l'enregistrement polarographique qu'on condui
de la manière décrite au paragraphe précédent.

La Fig. 1 représente les caractéristiques de la courbe de désamalgamation obtenue
partir d'une liqueur stanneuse contenant 0.8 μg de Sn par ml dans les condition
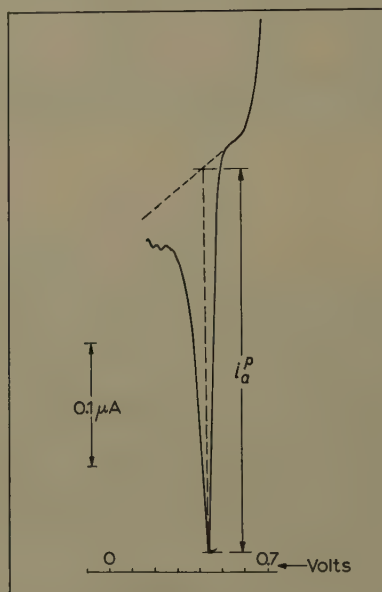opératoires citées plus haut.

Fig. 1.

Le Tableau I rassemble les valeurs des courants de pics de dissolution obtenus dan
un essai conduit en fonction de la concentration en acétate de triphényl-étain; l
courant résiduel a été préalablement soustrait des valeurs mesurées.

TABLEAU I

Concentrations μg/25 ml[a]	i_a^p μA	$i_a^p/c \cdot 10^3$	Écart % sur la moyenne	
20	0.075	3.75	5.04	
40	0.138	3.45	3.36	
60	0.212	3.53	1.12	
80	0.288	3.60	0.84	
100	0.354	3.54	0.84	$\overline{M} = 3.57$

[a] L'acétate de triphényl-étain contient 29% d'étain métal.

La précision est supérieure à celle de la polarographie classique utilisée dans l
domaine des faibles concentrations.

En prolongeant le temps de pré-électrolyse et en agitant les solutions on peu
observer que la limite de sensibilité est abaissée vers 0.2 μg/25 ml en acétate de tr

hényl-étain, soit 150 fois moins que la limite qu'on obtient suivant GORBACH ET
OCK[4]. Cet accroissement considérable de sensibilité souligne l'intérêt exceptionnel
e l'électrode à goutte pendante de mercure.

RÉSUMÉ

ar utilisation d'une électrode à goutte pendante de mercure (suivant VOGEL), les auteurs observent
e considérable amélioration de sensibilité dans le dosage de traces résiduaires d'acétate de
iphényl-étain, fongicide utilisé sur matériel végétal.

SUMMARY

sing a hanging dropping mercury electrode (according to VOGEL) the authors find a better
ensitivity of measurements in the determination of triphenyl tin acetate as fungicide residues
n vegetable matter.

ZUSAMMENFASSUNG

ei der polarographischen Bestimmung von Triphenylzinn-acetat (Schädlingsbekämpfungsmittel)
Pflanzenmaterial erreicht man eine höhere Empfindlichkeit der Messungen durch Anwendung
ner hängenden Quecksilbertropfelektrode.

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AMPEROMETRIC ARGENTIMETRIC AND MERCURIMETRIC TITRATION OF SULFHYDRYL

II. MERCURIMETRIC TITRATION

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In Part I of this investigation[1] data were presented on the high results obtained in the argentimetric amperometric titration of some sulfhydryl compounds containing active groups like carboxyl and amino which are responsible for extra binding of silver by silver mercaptides. The errors were found to be considerably decreased in the presence of a large excess of sulfite. For example, with thioglycolic acid the error was eliminated in the presence of 0.1 M sulfite. Use of this was made in the argenti metric titration of the disulfide of thioglycolic acid.

Sulfhydryl groups form mercaptides with mercury(II) which are much more stable than the corresponding silver mercaptides, and the mercury mercaptides are considerably less dissociated than the corresponding silver compounds[2]. Several sul hydryl compounds have been titrated at the rotated platinum wire electrode (RPtWE) with mercuric chloride or acetate[3]. In addition to the formation of normal mercaptide (XS)$_2$Hg end-points have been obtained corresponding to (XS)$_2$Hg$_2$ with thiol compounds containing reactive groups. The simple mercurimetric titration method could not be applied to the determination of disulfides in the presence of an excess of sulfite because the sulfite shifts the reduction of excess of mercury(II) (present as sulfito complex) at the RPtWE to such negative potentials that the mercury mercaptide is reduced before the excess of reagent. Thus it is impossible to detect an end-point at the RPtWE. On the other hand, at the dropping mercury electrode (DME) the sulfito complex of mercury(II) is reduced at potentials considerably more positive than the mercury mercaptides are and the end-point is easily detected[4]. The DME has a much smaller sensitivity than the RPtWE and is not as simple to work with as the latter. As a simple substitute for the DME it has been proposed[5] to use a rotated mercury pool electrode (RMPE) which appears to be very suitable for the ampero metric mercurimetric titration of sulfhydryl and of disulfide groups in bovine serum albumin[5]. In our present studies it appeared that, contrary to the behavior at the DME, sulfite shifts the excess mercury wave at the RMPE to such negative potential that at pH greater than 7 low molecular weight mercury mercaptides became reduced before the excess of mercury and no amperometric end-point could be determined. Apparently, a film is formed with time of standing on the surface of the electrode (RMPE, RPtWE) in solutions containing mercury(II) and sulfite and this film interferes with the reduction of the sulfito complex. No such film is formed at the DME because of the continuous formation of a fresh mercury surface.

In the present paper we have investigated the conditions under which some low molecular weight thiol compounds can be titrated accurately with mercury(II) by the amperometric technique using the RMPE as indicator electrode, and the results have been compared with those obtained at the RPtWE.

In connection with an extensive study of the equilibrium constant of the reaction of a disulfide XSSX with sulfite at varying pH

$$XSSX + SO_3^{-2} = XSSO_3^- + XS^- \tag{1}$$

it was necessary to titrate the sulfhydryl (XS$^-$) formed at pH 2 where the rate of the backward reaction is negligibly small. It is shown in this paper that under specified conditions the amperometric mercurimetric titration of sulfhydryl can be carried out accurately at pH 2 at the RMPE, even when the total sulfur dioxide concentration is 10^{-2} M. We have applied the method to the above equilibrium studies, the results of which will be reported elsewhere. The titration at pH 2 can also be made use of in the simple determination of disulfides (vide infra).

EXPERIMENTAL

Materials used

Mercuric nitrate, Hg(NO$_3$)$_2 \cdot$ H$_2$O, was a Baker A.R. product. Stock solutions were standardized against pure potassium thiocyanate. Mercuric chloride was a Merck reagent grade product. Other materials and experimental methods have been described in Part I[1].

The RMPE described by KOLTHOFF et al.[5] was used. In general an uncoated RPtWE was used. Titrations of glutathione were also carried out with a mercury-coated electrode.

RESULTS
Cysteine (RSH)

At RPtWE

Results of titrations of very dilute cysteine solutions which were 0.05 M in borax and 0.1 M in KCl (pH 9.15) are shown in Table I. Only one end-point was obtained corresponding to the formation of a compound in which cysteine and mercury are present in a molar ratio 1 : 1. Accuracy and precision were within one percent and
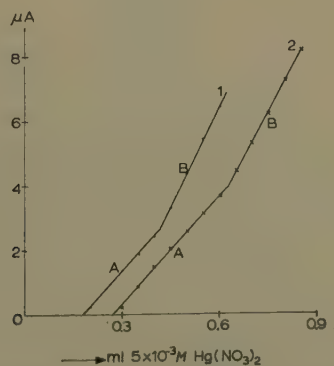
Fig. 1. Titration of cysteine with Hg(NO$_3$)$_2$ at RPtWE in acetate buffer pH 5.1, $E_{applied}$ = —0.2 V; (1) $4 \cdot 10^{-5}$ M RSH; (2) $6 \cdot 10^{-5}$ M RSH.

TABLE I

TITRATION OF CYSTEINE (RSH) WITH MERCURY(II) AT CLEAN RPtWE

Molarity	Buffer	pH	Addition of chloride	E_{appl} vs. SCE	Reagent	Molarity of reagent	Molar ratio RSH to Hg at end-point	RSH taken mg	RSH found mg	Error %
$3.3 \cdot 10^{-5}$	0.05 M borax	9.1	0.1 M KCl	—0.2	$HgCl_2$	$2 \cdot 10^{-3}$	1 : 1	0.1211	0.122	—1.0
$5 \cdot 10^{-5}$	0.05 M borax	9.1	0.1 M KCl	—0.2	$HgCl_2$	$2 \cdot 10^{-3}$	1 : 1	0.182	0.184	—1.3
$6.7 \cdot 10^{-5}$	0.05 M borax	9.1	0.1 M KCl	—0.2	$HgCl_2$	$2 \cdot 10^{-3}$	1 : 1	0.242	0.241	—0.5
$4 \cdot 10^{-5}$	0.1 M CH$_3$COONa–0.1 M CH$_3$COOH	5.1	—	—0.2	$Hg(NO_3)_2$	$5 \cdot 10^{-3}$	1 : 1	0.242	0.249	+2.5
$6 \cdot 10^{-5}$	0.1 M CH$_3$COONa–0.1 M CH$_3$COOH	5.1	—	—0.2	$Hg(NO_3)_2$	$5 \cdot 10^{-3}$	1 : 1	0.364	0.376	+3.3
10^{-4}	0.1 M CH$_3$COONa–0.1 M CH$_3$COOH	5.1	—	—0.2	$Hg(NO_3)_2$	10^{-2}	1 : 1	0.606	0.617	+2.0
$9.6 \cdot 10^{-5}$	0.01 M HNO$_3$	2.2	—	0.0	$Hg(NO_3)_2$	$5 \cdot 10^{-3}$	2 : 1	0.578	0.564	—2.5
$1.4 \cdot 10^{-4}$	0.01 M HNO$_3$	2.2	—	0.0	$Hg(NO_3)_2$	$5 \cdot 10^{-3}$	2 : 1	0.867	0.852	—1.5
$1.9 \cdot 10^{-4}$	0.01 M HNO$_3$	2.2	—	0.0	$Hg(NO_3)_2$	$5 \cdot 10^{-3}$	2 : 1	1.156	1.125	—2.5
$2.9 \cdot 10^{-4}$	0.01 M HNO$_3$	2.2	—	0.0	$Hg(NO_3)_2$	$5 \cdot 10^{-3}$	2 : 1	1.74	1.70	—2.3
10^{-4}	0.01 M HCl	2.2	—	0.0	$HgCl_2$	$5 \cdot 10^{-3}$	2 : 1	0.606	0.597	—1.5
$2 \cdot 10^{-4}$	0.01 M HCl	2.2	—	0.0	$HgCl_2$	$5 \cdot 10^{-3}$	2 : 1	1.212	1.212	0.0
$3 \cdot 10^{-4}$	0.01 M HCl	2.2	—	0.0	$HgCl_2$	$5 \cdot 10^{-3}$	2 : 1	1.818	1.791	—1.5

the same order of magnitude as those reported in a previous paper[3]. Titrations of cysteine with mercuric nitrate in an acetate buffer (pH 5.1) yielded two end-points corresponding to the formation of the mercaptides $(RS)_2Hg$ and $(RS)_2Hg_2$. The results reported in Table I refer to the second end-point which is taken as the point of inter-section of lines A and B in Fig. 1. At pH 5 the error was $+2.5 \pm 0.5\%$. Similar results (-0.7 to $+2.6\%$) were reported previously[3]. The first end-point cannot be determined accurately.

Titration results of cysteine with mercuric nitrate in a medium of 0.01 N nitric acid at a potential of 0.0 V are also presented in Table I. At this low pH the end-point corresponds to the formation of the compound $(RS)_2Hg$. Current–potential curves of mixtures of cysteine and mercuric nitrate in 0.01 N nitric acid are illustrated in Fig. 2.
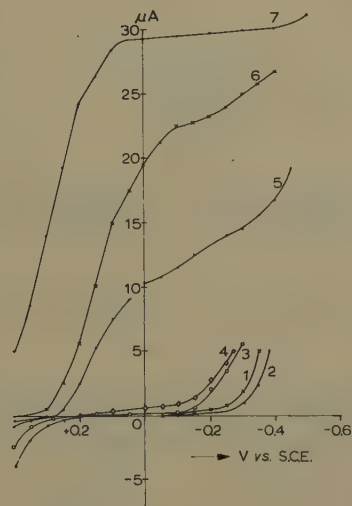
Fig. 2. Voltammograms in 0.01 M HNO$_3$ and $1.91 \cdot 10^{-4}$ M RSH at RPtWE. (1) 0.01 M HNO$_3$; (2) $1.91 \cdot 10^{-4}$ M RSH; (3) $1.91 \cdot 10^{-4}$ M RSH $+ 4.8 \cdot 10^{-5}$ M Hg(NO$_3$)$_2$; (4) $+ 9.55 \cdot 10^{-5}$ M Hg(II); (5) $+1.43 \cdot 10^{-4}$ M Hg(II); (6) $+1.91 \cdot 10^{-4}$ M Hg(II); (7) no RSH, $0.96 \cdot 10^{-4}$ M Hg(II).

Cysteine alone does not affect the residual current before the hydrogen reduction starts (curves 1 and 2 in Fig. 2). A reduction wave of $(RS)_2Hg$ is observed to start at about -0.15 V. When mercury is present in excess over $(RS)_2Hg$ some of the reagent is bound loosely to $(RS)_2Hg$ and the reduction wave of this excess of mercury starts at a more negative potential (about $+0.2$ V, see curves 5 and 6) as compared to that of "free" mercuric nitrate alone (curve 7), which starts at $+0.45$ V. The diffusion current of the "free" mercury (curve 7) is about 1.5 times greater than the limiting current of an excess of mercury of the same concentration. This limiting current of the excess of mercury is not well defined. A straight "excess reagent line" was found when the titration was carried out at a potential of 0.00 V (vs. SCE). The accuracy was $-2 \pm 0.5\%$ (Table I).

Current–potential curves were also determined in 0.01 N hydrochloric acid instead of nitric acid. The relations were found very much the same as in Fig. 2, except that the reduction wave of "free" mercuric chloride starts at $+0.25$ V instead of at $+0.45$ V

TABLE II

TITRATION OF CYSTEINE (RSH) WITH MERCURY(II) AT RMPE

$(RS)_2Hg$ at end-point

Molarity of RSH	Buffer	pH	Addition of chloride	E_{expt} vs. SCE	Reagent	Molarity of reagent	RSH taken mg	RSH found mg	Error %
10^{-4}	0.05 M borax	9.1	0.5 M KCl	—0.25	$HgCl_2$	10^{-2}	0.606	0.593	—2.0
$2 \cdot 10^{-4}$	0.05 M borax	9.1	0.5 M KCl	—0.25	$HgCl_2$	10^{-2}	1.211	1.188	—2.0
$3 \cdot 10^{-4}$	0.05 M borax	9.1	0.5 M KCl	—0.25	$HgCl_2$	10^{-2}	1.817	1.795	—1.2
$4 \cdot 10^{-4}$	0.05 M borax	9.1	0.5 M KCl	—0.25	$HgCl_2$	10^{-2}	2.423	2.375	—2.0
10^{-4}	0.1 M NH_4NO_3-0.04 M NH_3	9.0	—	—0.25	$Hg(NO_3)_2$ or $HgCl_2$	10^{-2}	0.606	0.594	—2.0
$2 \cdot 10^{-4}$	0.1 M NH_4NO_3-0.04 M NH_3	9.0	—	—0.25	$Hg(NO_3)_2$ or $HgCl_2$	10^{-2}	1.211	1.220	+0.6
$4 \cdot 10^{-4}$	0.1 M NH_4NO_3-0.04 M NH_3	9.0	—	—0.25	$Hg(NO_3)_2$ or $HgCl_2$	10^{-2}	2.423	2.447	+1.0
$6 \cdot 10^{-4}$	0.1 M NH_4NO_3-0.04 M NH_3	9.0	—	—0.25	$Hg(NO_3)_2$ or $HgCl_2$	10^{-2}	3.634	3.58	—1.3
10^{-4}	0.04 M phosphate	7.0	0.4 M KCl	—0.2	$HgCl_2$	10^{-2}	0.606	0.593	—2.0
$2 \cdot 10^{-4}$	0.04 M phosphate	7.0	0.4 M KCl	—0.2	$HgCl_2$	10^{-2}	1.211	1.182	—2.4
$4 \cdot 10^{-4}$	0.04 M phosphate	7.0	0.4 M KCl	—0.2	$HgCl_2$	10^{-2}	2.423	2.39	—1.0
$6 \cdot 10^{-4}$	0.04 M phosphate	7.0	0.4 M KCl	—0.2	$HgCl_2$	10^{-2}	3.634	3.634	0.0
$1.15 \cdot 10^{-4}$	0.01 M HNO_3	2.2	—	+0.25	$Hg(NO_3)_2$	$5 \cdot 10^{-3}$	0.695	0.703	+1.1
$1.5 \cdot 10^{-4}$	0.01 M HNO_3	2.2	—	+0.25	$Hg(NO_3)_2$	$5 \cdot 10^{-3}$	0.926	0.920	—0.6
$1.9 \cdot 10^{-4}$	0.01 M HNO_3	2.2	—	+0.25	$Hg(NO_3)_2$	$5 \cdot 10^{-3}$	1.157	1.15	—0.5
$3.8 \cdot 10^{-4}$	0.01 M HNO_3	2.2	—	+0.25	$Hg(NO_3)_2$	10^{-2}	2.315	2.325	+0.5
10^{-4}	0.01 M HCl	2.2	—	+0.05	$Hg(NO_3)_2$	10^{-2}	0.606	0.606	0.0
$2 \cdot 10^{-4}$	0.01 M HCl	2.2	—	+0.05	$Hg(NO_3)_2$	10^{-2}	1.211	1.223	+1.0
$6 \cdot 10^{-4}$	0.01 M HCl	2.2	—	+0.05	$Hg(NO_3)_2$	$2.5 \cdot 10^{-2}$	2.423	2.40	—0.9
10^{-3}	0.01 M HCl	2.2	—	+0.05	$Hg(NO_3)_2$	$2.5 \cdot 10^{-2}$	6.06	6.06	0.0

r mercuric nitrate. Titrations in 0.01 N hydrochloric acid could be carried out success-
lly with mercuric chloride as reagent at an applied potential of 0.0 V (see Table I).

RMPE

Only one end-point was obtained corresponding to the formation of $(RS)_2Hg$ in
ercurimetric titrations of cysteine at the RMPE under the conditions studied. Before
e end-point anodic cysteine currents are observed at the RMPE at pH between
and 2 while no anodic currents occur at the RPtWE.

In the amperometric titrations at the RMPE the end-point was always taken as
e point of intersection of the excess reagent line with the "base" line which is a
orizontal line, the ordinate of which is equal to the residual current of the supporting
ectrolyte. In practically all cases this residual current was equal to 0 to 0.1 μA and
sually could be neglected. The above method of end-point determination is preferred
ver the determination of the point of intersection between the anodic (XSH) current
ne before the end-point and the excess reagent line because the anodic current line
ften is not straight, the deviation being caused by film formation (vide infra, see
so Fig. 7).
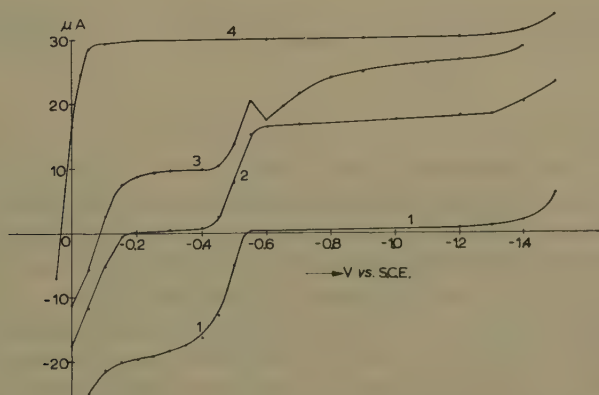
ig. 3. Voltammograms in 0.1 M NH$_4$NO$_3$, 0.1 M NH$_3$ at RMPE. (1) $2 \cdot 10^{-4}$ M RSH; (2) $2 \cdot 10^{-4}$ M
RSH $+$ 10^{-4} M Hg(NO$_3$)$_2$; (3) $+1.4 \cdot 10^{-4}$ M Hg(NO$_3$)$_2$; (4) no RSH, 10^{-4} M Hg(NO$_3$)$_2$.

The current potential curves in Fig. 3 were measured at pH 9. Free cysteine gives
n anodic wave with a clearly defined diffusion current which is proportional to its
oncentration (curve 1). When mercury(II) and cysteine are present in a molar ratio
:2, the anodic wave of cysteine has disappeared and only the mercaptide reduction
ave is observed (curve 2). On further addition of mercury(II) the excess mercury(II)
ave is observed which starts at a potential about 0.1 V more negative than that
bserved for the free mercury ammine ions (curves 3 and 4). In the presence of excess
f mercury the mercuric cysteinate wave starts to exhibit irregularities (curve 3).
At a potential of —0.25 V the excess reagent line yields a straight line and the titration
an be carried out successfully with mercuric nitrate or chloride (see Table II). Excess
hloride does not interfere.

Equally good results were obtained in a borax buffer (pH 9) or phosphate buffer
pH 7) even at chloride concentrations as great as 0.5 M (Table II).

Current–potential curves in 0.01 M nitric acid are presented in Fig. 4. The fr[...]
mercaptan wave (curve 1) and the mercaptide wave (curve 2) are shifted about 0.4 [...]
to more positive potentials as compared to the potentials observed at pH 9. This [...]
effect was expected. The mercaptide wave decreases in height when there is mercu[...]
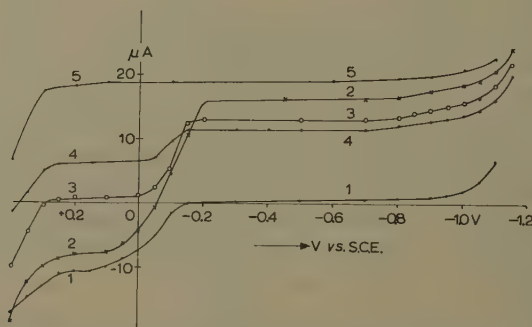in excess over $(RS)_2Hg$ in the solution (compare curves 3 and 4 in Fig. 4). Th[...]

Fig. 4. Voltammograms with RSH in 0.01 M HNO₃ at RMPE. (1) $1.9 \cdot 10^{-4}$ M RSH; (2) 10^{-4} [...]
Hg(NO₃)₂ + $2.86 \cdot 10^{-4}$ M RSH; (3) + $1.9 \cdot 10^{-4}$ M RSH; (4) + $0.95 \cdot 10^{-4}$ M RSH; (5) no RS[...]
10^{-4} M Hg(NO₃)₂.

combined with the fact that the "excess" mercury waves start at $+0.38$ V as con[...]
pared to $+0.42$ V for free mercury (curve 5) and that the limiting current of the exce[...]
mercury is smaller than that of an equal concentration of free mercury, gives stron[...]
indication of reaction to occur between $(RS)_2Hg$ and $Hg(II)$. The excess of mercur[...]
yields a straight line at an applied potential of $+0.25$ V and good results are obtaine[...]
in the amperometric titration at this potential (see Table II).

Current–potential curves were also run at pH 2 in the presence of varying con[...]
centrations of chloride. From these it was concluded that good results could be ob[...]
tained in titrations in 0.01 M chloride at pH 2 at an applied potential of $+0.05$ V[...]
This was confirmed by actual experiments which are reported in Table II.

Reduced glutathione (GSH)

At RPtWE

Titrations of glutathione were carried out in borax buffer in the presence an[...]
absence of chloride. In titrations carried out using a mercury-coated electrode[3] tw[...]
breaks were observed corresponding to the formation of $(RS)_2Hg$ and $(RS)_2Hg_2$. Onl[...]
the second can be found with some degree of accuracy. The current observed betwee[...]
the two breaks is decreased in the presence of chloride. From the results in Table II[...]
it appears that the error at the second break corresponding to $(GS)_2Hg_2$ is $+4.5 \pm$[...]
0.5% in the absence of chloride and $-1.5 \pm 0.5\%$ in the presence of 0.1 M chlorid[...]
Presence of chloride is definitely beneficial at this pH. Some titrations of glutathion[...]
in 0.05 M borax were also carried out using an uncoated platinum electrode. Result[...]
accurate to $-0.8 \pm 0.5\%$ were obtained in the concentration range between $6 \cdot 10^{-}$[...]
and $3 \cdot 10^{-4}$ M in GSH. Chloride in a concentration of 0.1 M did not affect the result[...]
With increasing concentration of glutathione the negative error became considerabl[...]

TABLE III

RATION OF GLUTATHIONE (GSH) WITH MERCURIC NITRATE IN 0.05 M BORAX BUFFER AT RPtWE

$E_{applied} = -0.2$ V; $(GS)_2Hg_2$ at end-point

Molarity of GSH	Addition of chloride	Molarity of reagent	GSH taken mg	GSH found mg	Error %	RPtWE
$5 \cdot 10^{-5}$	—	10^{-2}	0.768	0.799	+ 4.0	coated
10^{-4}	—	10^{-2}	1.536	1.613	+ 5.0	coated
$2 \cdot 10^{-4}$	—	10^{-2}	3.073	3.233	+ 5.2	coated
$4 \cdot 10^{-4}$	—	10^{-2}	6.146	6.392	+ 4.0	coated
$5 \cdot 10^{-5}$	0.1 M KCl	10^{-2}	0.768	0.783	— 2.0	coated
10^{-4}	0.1 M KCl	10^{-2}	1.536	1.527	— 0.6	coated
$2 \cdot 10^{-4}$	0.1 M KCl	10^{-2}	3.073	3.13	— 2.0	coated
$4 \cdot 10^{-4}$	0.1 M KCl	10^{-2}	6.146	6.20	+ 0.5	coated
$6 \cdot 10^{-5}$	—	10^{-2}	0.921	0.921	0.0	clean
10^{-4}	—	10^{-2}	1.536	1.521	— 1.0	clean
$2 \cdot 10^{-4}$	—	10^{-2}	3.073	3.043	— 1.0	clean
$3.5 \cdot 10^{-4}$	—	$2.5 \cdot 10^{-2}$	5.376	4.812	—10.5	clean
$5 \cdot 10^{-4}$	—	$2.5 \cdot 10^{-2}$	7.68	7.26	— 5.5	clean
10^{-3}	—	$5 \cdot 10^{-2}$	15.36	13.82	—10.0	clean
$6 \cdot 10^{-5}$	0.1 M KCl	10^{-2}	0.921	0.921	0.0	clean
$2 \cdot 10^{-4}$	0.1 M KCl	10^{-2}	3.073	3.027	— 1.5	clean
$5 \cdot 10^{-4}$	0.1 M KCl	$5 \cdot 10^{-2}$	7.68	7.22	— 6.0	clean
$7.5 \cdot 10^{-4}$	0.1 M KCl	$5 \cdot 10^{-2}$	11.52	9.79	—15.0	clean

olutions which were $3.5 \cdot 10^{-4}$, $5 \cdot 10^{-4}$ and 10^{-3} M in GSH were titrated with negative rrors of 10.5, 5.5 and 10.0% respectively. These titrations were carried out relatively apidly. Shortly after the end-point in the titration of 10^{-3} M glutathione the current ontinued to rise and after a few minutes the observed value became considerably reater than the current measured immediately after addition of excess of mercury. his effect is caused by coating of the electrode with $(GS)_2Hg_2$ during the titration. itrations of $5 \cdot 10^{-4}$ and $7.5 \cdot 10^{-4}$ M GSH carried out in the presence of 0.1 M chloride ielded a negative error of 6 and 15% respectively (Table III).

INGRAM[6] reports good results in the titration in an ammonia buffer of pH 9.2. URTON[7] could confirm this, but also mentions an increasing positive error with ncreasing or decreasing pH. He reports an error of +30% both at pH of 7 and of 10.5. Ve have carried out titrations in ammonia buffers and did not observe a sharply efined end-point. The current at the end-point [$(GS)_2Hg_2$] was relatively large and he error fluctuated widely. Titration in borax medium in the presence of chloride preferred at GSH concentrations of $2 \cdot 10^{-4}$ M or less. Quite generally, the argenti-netric titration of GSH is preferred over the mercurimetric one.

Two breaks were also observed in an acetate buffer of pH 5.4 which was 0.12 M n sodium acetate and 0.02 M in acetic acid. In the titration at -0.1 V of $6 \cdot 10^{-5}$, $\cdot 10^{-4}$ and $2 \cdot 10^{-4}$ M GSH the errors were +1.0, 0.0 and -2.0% respectively. Again he end-point corresponds to a composition of $(GS)_2Hg_2$.

Titrations were also carried out in 0.01 N nitric acid at 0.0 V and again two breaks vere observed. The second break is fairly well defined, but the current is already elatively large between the first and the second break. Using a clean electrode $4 \cdot 10^{-5}$ o $10 \cdot 10^{-5}$ M GSH solutions were titrated with an accuracy of ± 1%.

At RMPE

Current–potential curves of GSH in mixtures with mercuric nitrate in 0.05 M bor
solutions at the RMPE are illustrated in Fig. 5. The anodic GSH waves are clea
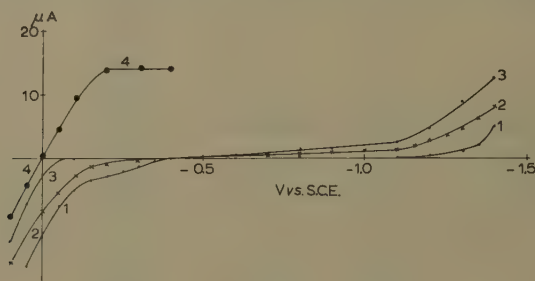noticeable (curves 1 and 2) as long as the mole ratio of GSH to Hg(II) is greater than

g. 5. Voltammograms of GSH in 0.05 M borax at RMPE. (1) $2 \cdot 10^{-4}$ M GSH; (2) $2 \cdot 10^{-4}$
GSH + $0.5 \cdot 10^{-4}$ M Hg(NO₃)₂; (3) + 10^{-4} M Hg(NO₃)₂; (4) + $1.5 \cdot 10^{-4}$ M Hg(NO₃)₂.

However there is no diffusion plateau on the GSH waves. Peculiarly enough
reduction waves of mercury glutathionate are observed, although these are w
developed at the dropping mercury electrode. The abnormal behaviour is attribut
to the formation of a greyish-black film of mercury mercaptide on the surface of t
mercury which interferes with the mercury mercaptide reduction but apparently n
with the reduction of excess of mercuric nitrate (see curve 4 in Fig. 5). Amperometr
titrations of 10^{-4} to $4 \cdot 10^{-4}$ M GSH in borax medium were carried out at a potential
—0.2 V with an accuracy of —1 ± 1%. It should be noted that the reagent line do
not become straight until an excess of 25% has been added under these condition

The end-point is sharply defined and corresponds to a composition of (GS)₂Hg an
not to (GS)₂Hg₂ as found at the RPtWE. Apparently the loosely bound mercury,
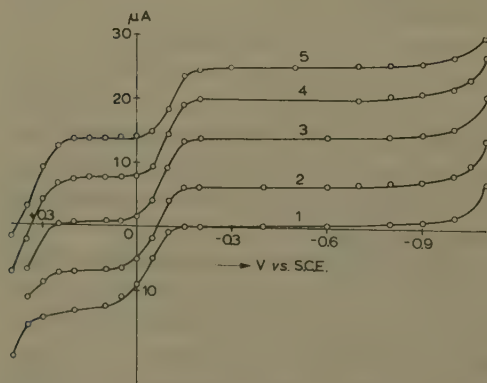
Fig. 6. Voltammograms of GSH in 0.014 N HNO₃.
(1) 0.014 N HNO₃ + $2 \cdot 10^{-4}$ M GSH; (2) + $5 \cdot 10^{-5}$
M Hg(NO₃)₂; (3) + 10^{-4} M Hg(NO₃)₂; (4) + $1.5 \cdot 10^{-4}$ M Hg(NO₃)₂; (5) + $2 \cdot 10^{-4}$ M Hg(NO₃)₂.
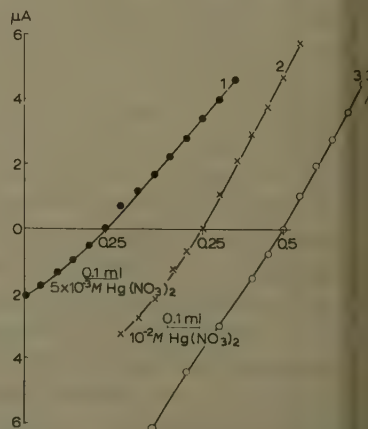
Fig. 7. Titration of GSH in 0.012
HNO₃ at RMPE. $E_{applied}$ = +0
V. (1) $5 \cdot 10^{-5}$ M GSH; (2) $1 \cdot 10^{-4}$
GSH; (3) $2 \cdot 10^{-4}$ M GSH.

cess over $(GS)_2Hg$, is reduced at the RMPE. From the analytical view point again,
e argentimetric titration is preferred at pH 9.

In 0.014 N nitric acid the anodic GSH waves and the mercury glutathionate waves
e well defined as illustrated in Fig. 6. The anodic GSH waves disappear when the
ble ratio of GSH to Hg(II) becomes equal or smaller than 2. At a smaller ratio than
he excess mercury wave appears to start at potentials more positive than $+0.3$ V.
The amperometric titration of GSH at pH 2 and an applied potential of $+0.1$ V
elds good results. Some examples of titration lines are given in Fig. 7. It is seen that
e anodic GSH line before the end-point is not exactly a straight line. This is the
ason why the end-point is taken as the point of intersection between the "base"
e and the excess reagent line, as mentioned in an earlier section. In the titration of
$5 \cdot 10^{-5}$, $1 \cdot 10^{-4}$, $2 \cdot 10^{-4}$ and $4 \cdot 10^{-4}$ M GSH the error was 0, 0, —2, and —2.5%
spectively. As is shown in a later section the titration gives excellent results at pH 2
the presence of 0.01 M sulfur dioxide.

Thioglycolic acid (TSH)

RPtWE

In the titrations of thioglycolic acid with mercuric nitrate in ammonia or borax
ffers only one end-point was observed corresponding to the formation of the mer-
ptide $(TS)_2Hg$. Chloride did not affect the accuracy. However, in borax buffers
the presence of chloride it was necessary to wait after the end-point for two minutes
fore the excess mercury current became constant. This effect of chloride was not
bserved in ammonia buffers which are preferred as titration media. From the results
Table IV it appears that the titration yields satisfactory results.

RMPE

Voltammograms of mixtures of thioglycolic acid and mercuric nitrate in 0.05 M
orax solutions greatly resemble those observed with glutathione (see Fig. 5). Again,

TABLE IV

TRATION OF THIOGLYCOLIC ACID (TSH) WITH MERCURIC NITRATE IN BORAX AND AMMONIA BUFFERS
AT RPtWE

End-point $(TS)_2Hg$. $E_{applied}$ = —0.2 V

Molarity of TSH	Buffer	pH	Molarity of reagent	TSH taken mg	TSH found mg	Error %
$2 \cdot 10^{-4}$	0.05 M borax	9.1	10^{-2}	0.921	0.939	$+1.0$
$5 \cdot 10^{-4}$	0.05 M borax	9.1	10^{-2}	2.303	2.33	$+1.2$
10^{-3}	0.05 M borax	9.1	$5 \cdot 10^{-2}$	4.606	4.66	—1.4
$2 \cdot 10^{-3}$	0.05 M borax	9.1	$5 \cdot 10^{-2}$	9.21	9.38	$+1.8$
$2 \cdot 10^{-4}$	0.05 M borax–0.1 M KCl	9.1	10^{-2}	0.921	0.921	0.0
$4 \cdot 10^{-4}$	0.05 M borax–0.1 M KCl	9.1	10^{-2}	1.84	1.89	$+2.5$
10^{-3}	0.05 M borax–0.1 M KCl	9.1	$5 \cdot 10^{-2}$	4.61	4.53	—1.6
$2 \cdot 10^{-4}$	0.2 M NH$_4$NO$_3$–0.1 M NH$_3$	9.0	10^{-2}	0.921	0.921	0.0
$4 \cdot 10^{-4}$	0.2 M NH$_4$NO$_3$–0.1 M NH$_3$	9.0	10^{-2}	1.84	1.88	$+2.0$
10^{-3}	0.2 M NH$_4$NO$_3$–0.1 M NH$_3$	9.0	$5 \cdot 10^{-2}$	4.61	4.57	—0.8
$2 \cdot 10^{-4}$	0.2 M NH$_4$Cl–0.1 M NH$_3$	9.0	10^{-2}	0.921	0.930	$+1.0$
$4 \cdot 10^{-4}$	0.2 M NH$_4$Cl–0.1 M NH$_3$	9.0	10^{-2}	1.84	1.90	$+3.0$
10^{-3}	0.2 M NH$_4$Cl–0.1 M NH$_3$	9.0	$5 \cdot 10^{-2}$	4.61	4.55	—1.2

film formation prevents the reduction of mercury thioglycolate, but not that of the mercury(II) in excess over $(TS)_2Hg$. A sharp end-point is observed in the titration in borax or ammonia buffers, like that at the RPtWE. Some results are given Table V.

TABLE V

TITRATION OF THIOGLYCOLIC ACID (TSH) WITH MERCURIC NITRATE AT RMPE IN 0.05 M BORAX BUFFER

End-point $(TS)_2Hg$, $E_{applied} = -0.2$ V

Molarity of TSH	Molarity of reagent	TSH taken mg	TSH found mg	Error %
10^{-4}	10^{-2}	0.461	0.464	—0.8
$2 \cdot 10^{-4}$	10^{-2}	0.921	0.925	+0.4
$5 \cdot 10^{-4}$	10^{-2}	2.30	2.33	—1.0
10^{-3}	$5 \cdot 10^{-2}$	4.61	4.65	—1.0
$2 \cdot 10^{-3}$	$5 \cdot 10^{-2}$	9.21	9.28	+0.7

In 0.01 to 0.015 N nitric acid the voltammograms are very similar to those of GSH until the mole ratio of TSH to Hg(II) becomes smaller than 2.0. From then on the mercury mercaptide wave decreases with increasing excess of mercury and the wave exhibits maxima and shows minima and other irregularities. Also the excess of reagent wave becomes somewhat irregular. Apparently, film formation accounts for the irregularities which disappear when the solution is also 0.01 M in sulfur dioxide (vide infra). In the absence of sulfur dioxide the amperometric titration at pH 2 does not yield good results.

2-Mercaptoethanol (ESH)

At RPtWE

2-Mercaptoethanol in borax or ammonia buffers behaves towards mercury(II) the RPtWE like thioglycolic acid and there is only one break, the end-point corresponding to $(ES)_2Hg$. As is seen from Table VI the accuracy and precision of the results are $+1 \pm 1\%$.

At RMPE

As is clear from the results in Table VII, solutions buffered with borax or ammonia can be titrated with an error of $-0.8 \pm 0.5\%$. Solutions acidified with nitric acid to pH 2 which were $4 \cdot 10^{-4}$ to $2 \cdot 10^{-3}$ M in ESH were titrated with an error of -2

TABLE VI

TITRATION OF 2-MERCAPTOETHANOL (ESH) WITH 0.01 M MERCURIC NITRATE IN 0.05 M BORAX BUFFER AT RPtWE

End-point $(ES)_2Hg$, $E_{applied} = -0.2$ V

Molarity of ESH	ESH taken mg	ESH found mg	Error %
$5.1 \cdot 10^{-5}$	0.198	0.203	+2.5
$1.01 \cdot 10^{-4}$	0.396	0.398	+0.5
$2.03 \cdot 10^{-4}$	0.792	0.802	+1.3
$4.06 \cdot 10^{-4}$	1.58	1.61	+1.7
$8.1 \cdot 10^{-4}$	3.17	3.25	+2.5

o.3%. At pH 9 as well as at pH 2 the end-point was found to correspond to the
mposition $(ES)_2Hg$.

TABLE VII

TITRATION OF 2-MERCAPTOETHANOL (ESH) WITH MERCURIC NITRATE AT RMPE
End-point $(ES)_2Hg$

Molarity of ESH	Buffer	pH	E_{appt} vs. SCE	Molarity of reagent	ESH taken mg	ESH found mg	Error %
$5 \cdot 10^{-5}$	0.05 M borax	9.1	—0.2	10^{-2}	0.195	0.195	0.0
10^{-4}	0.05 M borax	9.1	—0.2	10^{-2}	0.391	0.386	—1.3
$2 \cdot 10^{-4}$	0.05 M borax	9.1	—0.2	10^{-2}	0.781	0.778	—0.4
$4 \cdot 10^{-4}$	0.05 M borax	9.1	—0.2	10^{-2}	1.56	1.55	—0.5
$8 \cdot 10^{-4}$	0.05 M borax	9.1	—0.2	10^{-2}	3.13	3.11	—0.5
$4 \cdot 10^{-4}$	0.01 M HNO$_3$	2.2	+0.1	10^{-2}	1.563	1.554	—0.6
10^{-3}	0.01 M HNO$_3$	2.2	+0.1	$5 \cdot 10^{-2}$	3.91	3.83	—2.0
$2 \cdot 10^{-3}$	0.01 M HNO$_3$	2.2	+0.1	$5 \cdot 10^{-2}$	7.81	7.84	+0.3

itration of the various thiol compounds at pH 2 in the presence of 0.01 M sulfur dioxide.
Application to disulfide determination

ow molecular weight disulfides can be determined by direct amperometric titration
ith silver in buffers of pH 8 to 9 in the presence of sufficient sulfite[8]. However, some
niols like cysteine give a wrong end-point in this argentimetric titration[1]. The titra-
on cannot be done mercurimetrically at pH 9 because no excess mercury line can
e found. On the other hand, it was shown that the thiol titration yields good results
t pH 2 in the presence of 0.01 M (total) sulfur dioxide at the RMPE. Results ob-
ained with the various thiols are presented in Table VIII.

Use of this can be made in a simple determination of disulfides, which is especially
dvantageous when the argentimetric titration yields erroneous results. To a solution
o⁻³ M or more dilute in disulfide in a borax or ammonia buffer add sodium sulfite
n a concentration of 0.01 M and enough standard mercuric nitrate or acetate to
orce reaction (1) quantitatively to the right. The forward reaction is very incomplete
t pH 9, but it is being made complete when mercuric nitrate is added in slight excess
ver the amount needed to bind all XS⁻. The solution is then acidified with nitric
cid to pH 2 (glass electrode) and titrated with mercury(II) solution at the RMPE
t +0.05 or +0.1 V.

The method was applied to the determination of cystine. The excess of mercuric
itrate added to the ammoniacal sulfite buffer was 3%. Titration results of cystine–
ulfite mixtures are listed in Table IX. Solutions which were $5 \cdot 10^{-5}$ to $3 \cdot 10^{-4}$ M in
RSSR were titrated with an error of +1%.

DISCUSSION

Vith the same reagent at a pH of 9 the end-point at the RPtWE is found for cysteine
RSH) and glutathione (GSH) at a mole ratio of RSH (and GSH) to mercury(II) of
: 1, while at the RMPE a well defined end-point is found at a mole ratio of 2 : 1.
he reason for this difference in results with the two electrodes is that $(RS)_2Hg$ and
GS)$_2$Hg bind more mercury(II), which is loosely bound[4] and which is completely reduc-

TABLE VIII

TITRATION IN 0.1 M SO$_2$ AT pH 2 AT RPME

End-point (XS)$_2$Hg

Molarity	Thiol	E_{appl} vs. SCE	Molarity of Hg(NO$_3$)$_2$	Thiol taken mg.	Thiol found mg	Error %
10^{-4}	GSH	+0.1	10^{-2}	1.536	1.566	+2.0
$2 \cdot 10^{-4}$	GSH	+0.1	10^{-2}	3.07	3.10	—1.0
$4 \cdot 10^{-4}$	GSH	+0.1	10^{-2}	6.15	6.15	0.0
$6 \cdot 10^{-4}$	GSH	+0.1	$5 \cdot 10^{-2}$	9.22	9.46	—2.6
$4 \cdot 10^{-5}$	RSH	+0.05	10^{-2}	0.242	0.242	0.0
10^{-4}	RSH	+0.05	10^{-2}	0.605	0.605	0.0
$2 \cdot 10^{-4}$	RSH	+0.05	10^{-2}	1.21	1.22	+0.6
$4 \cdot 10^{-4}$	RSH	+0.05	10^{-2}	2.42	2.43	+0.3
$6 \cdot 10^{-4}$	RSH	+0.05	10^{-2}	3.63	3.61	—0.7
$8 \cdot 10^{-4}$	RSH	+0.05	10^{-2}	4.85	4.81	—0.8
10^{-4}	TSH	+0.05	10^{-2}	0.461	0.468	+1.6
$5 \cdot 10^{-4}$	TSH	+0.05	10^{-2}	2.30	2.35	+2.0
10^{-3}	TSH	+0.05	$5 \cdot 10^{-2}$	4.61	4.62	—0.4
$2 \cdot 10^{-3}$	TSH	+0.05	$5 \cdot 10^{-2}$	9.21	9.31	+1.0
$2 \cdot 10^{-4}$	ESH	+0.1	10^{-2}	0.781	0.789	+1.0
$4 \cdot 10^{-4}$	ESH	+0.1	10^{-2}	1.56	1.575	+1.0
$8 \cdot 10^{-4}$	ESH	+0.1	10^{-2}	3.13	3.17	+1.2
$1.5 \cdot 10^{-3}$	ESH	+0.1	$5 \cdot 10^{-2}$	5.86	5.90	+0.7

TABLE IX

TITRATION OF CYSTINE ACCORDING TO PROCEDURE GIVEN IN THE TEXT WITH 0.01 M MERCURIC NITRATE AT RMPE

$E_{applied} = +0.05$ V

Molarity of RSSR	RSSR taken mg	RSSR found mg	Error %
$5 \cdot 10^{-5}$	0.600	0.600	0.0
10^{-4}	1.201	1.21	+0.8
$2 \cdot 10^{-4}$	2.403	2.427	+1.0
$3 \cdot 10^{-4}$	3.604	3.64	+1.1

ed at the applied potential at the RMPE but yields only small currents at the RPtWI A large increase in current at the platinum electrode is observed after formation c (RS)$_2$Hg$_2$ and (GS)$_2$Hg$_2$. With thioglycolic acid (TSH) and 2-ethanol mercaptan (ESH the end-point at both electrodes at pH 9 is found at a mole ratio of 2 TSH or 2 ESI to 1 Hg(II). At the (clean) platinum electrode no anodic current of the thiol compoun is observed at the applied potential, while at the RMPE an anodic current is observe before the end-point as illustrated in Fig. 7. In the first part of this study[1] it was state that the argentimetric amperometric titration at pH 9 of cysteine and of thioglycoli acid yield large positive errors. Particularly for these two compounds the titratio at the RMPE is recommended which yields excellent results over a wide range c concentrations.

The binding of more than one mercury(II) per two sulfhydryl groups occurs wit RSH, GSH and TSH, but not with ESH. The first three contain other functiona

roups (carboxyl, and also amino in RSH and GSH) which are responsible for further
mercury binding. We are continuing the argentimetric and mercurimetric studies with
everal other mercaptans in order to get further insight in the role of various functional
roups in the extra binding of silver and mercury by the normal mercaptides.

The disulfide determination by making the solution buffered at pH 9 with borax
r ammonia 0.01 M in sulfite followed by adding standard mercuric nitrate solution
n slight excess over $(XS)_2Hg$, acidifying with nitric acid to pH 2, and measuring the
xcess reagent line, is of special advantage in an assay of cystine. With this compound
he direct argentimetric titration yields high results[1]. For the determination of the
isulfides of GSH, TSH and ESH the direct ampero-argentimetric method is simpler
nd preferred.

In connection with our studies of the equilibrium constants between disulfides and
ulfite at varying pH it is gratifying that the equilibrium concentration of the thiol
ompounds can be titrated at pH 2 with mercuric nitrate at the RMPE. This method
ad been applied already to the determination of disulfide in denatured bovine serum
lbumin[5]. Here the situation is simpler than with low molecular weight thiol compounds
ecause the mercury mercaptides of albumin are not reduced at a RMPE.

SUMMARY

The ampero-mercurimetric titration of cysteine (RSH), glutathione (GSH), thioglycolic acid (TSH)
nd 2-mercaptoethanol (ESH) at the RMPE at pH 9 yields a sharply defined end-point correspond-
ng to the composition $(XS)_2Hg$. Under the same conditions with the RPtWE two breaks are
observed in the titration lines with RSH and GSH, corresponding to compositions $(RS)_2Hg$ and
RS)_2Hg_2 respectively. On the other hand, with TSH and ESH only one clear break is found at
he RPtWE corresponding to $(TS)_2Hg$ or $(ES)_2Hg$. Conditions have been described for the accurate
mercurimetric titration of the thiol compounds at pH 2 in the presence of 0.01 M sulfur dioxide
at the RMPE. Use of this can be made in the determination of disulfides and in the determination
of the equilibrium concentrations of the reaction between a disulfide and a sulfite at varying pH.

RÉSUMÉ

Les auteurs ont effectué une étude sur le titrage ampérométrique de la cystéine, de la glutathione,
de l'acide thioglycolique et du mercapto-2-éthanol, par mercurimétrie. Ils ont examiné également
e comportement des disulfures et la détermination des concentrations d'équilibre, à divers pH,
ntre disulfure et sulfite.

ZUSAMMENFASSUNG

Beschreibung einer ampero-mercurimetrischen Methode zur Bestimmung von Cystein, Glutathion,
Thioglycolsäure und 2-Mercapto-äthanol. Die Methode lässt sich verwenden zur Bestimmung von
Disulfiden und Gleichgewichtskonzentrationen bei der Reaktion zwischen einem Disulfid und
Sulfit bei verschiedenem pH.

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SPECTROPHOTOMETRIC DETERMINATION OF ALUMINIUM WITH STILBAZO

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Stilbazo (stilbene-4,4'-bis(1-azo-3,4'-dihydroxybenzene)-2,2'-disulfonate) has been proposed as a spectrophotometric reagent for aluminium[1]. The reagent has been used for the determination of aluminium in iron and steel[2,3].

In the present work the results of an investigation of stilbazo as a spectrophotometric reagent for aluminium are presented.

EXPERIMENTAL

Apparatus and solutions

Apparatus. A Beckman Spectrophotometer, Model DU, with 1-cm cells was used for the absorption measurements. The pH was measured with a Beckman H-2 type pH-meter.

Aluminium standard solution. 1.349 g of spectrographically pure aluminium was dissolved in hydrochloric acid and the solution was diluted to 1 l with distilled water. From this standard solution more dilute solutions were prepared as required.

Reagent solution. 0.120 g of stilbazo was dissolved in 1 l of distilled water.

Buffer solution. 24 g of sodium acetate trihydrate was dissolved in 1 l of distilled water. The pH was adjusted to 5.65 by dropwise addition of concentrated acetic acid.

Procedure

An aliquot of the aluminium standard solution was pipetted into a 25-ml volumetric flask and 5 ml of the reagent solution and 10 ml of the buffer solution were added. The solution was diluted to volume with distilled water and the absorption was measured against a reagent blank.

RESULTS AND DISCUSSION

Absorption curves

The absorption of the aluminium complex against both reagent solution and distilled water and that of the reagent solution against distilled water were measured as a function of wavelength. The values are plotted in Fig. 1. The absorption curve of the aluminium complex shows a maximum at 500 mμ and all subsequent measurements were made at that wavelength.

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Effect of pH, time, temperature and reagent concentration

Solutions of the reagent and solutions containing aluminium and reagent were adjusted to various pH values with sodium acetate–acetic acid buffer solutions. In Fig. 2 the absorption of the reagent solution and the absorption of the aluminium complex are plotted as a function of pH. The absorption of the aluminium complex
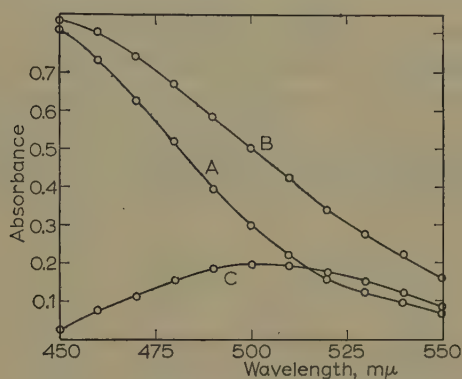
Fig. 1. Absorption spectra of reagent and its aluminium complex. A, Reagent against water; B, Reagent plus aluminium against water; C, Reagent plus aluminium against reagent.
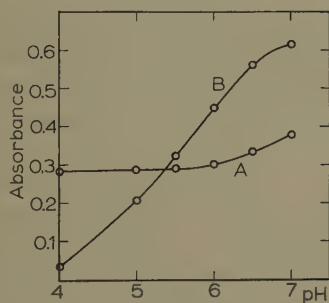
Fig. 2. A, Effect of pH on the reagent; B, Effect of pH on the complex.
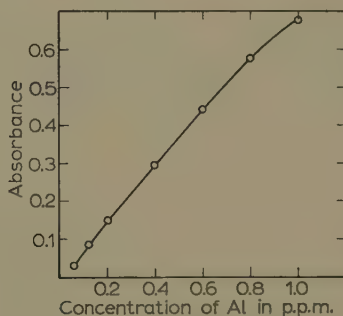
Fig. 3. Beer's law curve.

increased almost linearly in the range pH 4–7. The absorption of the reagent solution was approximately constant between pH 4 and 5.8. Above 5.8 the absorption increased.

The colour of the aluminium complex was found to be stable for at least 3 h. The colour remained unchanged under normal conditions of light and temperature (20–30°).

The absorption of the aluminium complex increased slightly with increasing reagent concentration. With sufficient excess of reagent it was, however, practically independent of the reagent concentration.

The buffer concentration did not affect the absorption of the complex up to about 0.25 g sodium acetate per 25 ml. Higher buffer concentrations caused decreasing colour intensities.

Beer's law

Different quantities of the aluminium standard solution were mixed with 10 ml of reagent and 10 ml of buffer solution. The solutions were diluted to 25 ml and their absorbancies were measured at 500 mμ against a reagent blank. Beer's law was found to be obeyed in the concentration range 0.1–0.8 p.p.m. aluminium. A slight deviation from Beer's law was found at lower and higher concentrations.

Composition, molar extinction coefficient and instability constant

The empirical formula of the coloured aluminium–stilbazo complex was determined by the method of "continuous variation" and by the "mole ratio" method. The results suggest a 1 : 1 complex of aluminium with the reagent.

The molar extinction coefficient of the complex was calculated to be 19,500. The instability constant calculated from the relationship[4]

$$K = \frac{\alpha^2 C}{1 - \alpha} \quad (\alpha = \frac{Em - Es}{Em})$$

was found to be equal to $5.96 \cdot 10^{-6}$.

Effect of foreign ions

Oxalate, tartrate, citrate, NTA, EDTA and fluoride interfered by bleaching the colour even in concentrations comparable with that of aluminium. Copper, tin(II), molybdenum(VI), tungsten(VI), titanium(IV), vanadium(IV) and (V) and iron(II) and (III) interfered by deepening the colour when present in 1:1 ratio with aluminium. Chromium(III) caused the colour to fade. Ions that could be tolerated in higher concentrations are listed in Table I.

TABLE I

TOLERANCES TO DIVERSE IONS
Aluminium concentration, 0.3 p.p.m.

Ion	P.p.m. tolerated	Ion	P.p.m. tolerated
Sn(IV)	30	Nb(V)	3
Co	300	As(III)	100
Ni	30	As(V)	10
Zn	30	Pb	30
Cd	30	Mn(II)	300
Ca	300	PO$_4$	5
Mg	300	Cl (as NaCl)	1000
Cr(VI)	4	SO$_4$ (as Na$_2$SO$_4$)	10000
		NO$_3$ (as NaNO$_3$)	1000
		NH$_4$ (as NH$_4$Cl)	1000

SUMMARY

The use of stilbazo as a spectrophotometric reagent for aluminium has been investigated. The reagent forms a stable coloured complex with aluminium showing an absorption maximum at 500 mμ. The system obeys Beer's law from 0.1–0.8 p.p.m. aluminium. The molar extinction coefficient and the stoichiometric composition of the coloured complex have been determined.

RÉSUMÉ

Les auteurs ont effectué une étude sur l'emploi du "stilbazo" comme réactif pour le dosage spectro-photométrique de l'aluminium. Le complexe formé est stable, avec maximum d'absorption à 500 mμ.

ZUSAMMENFASSUNG

Beschreibung einer Untersuchung über die Verwendung von "Stilbazo" als Reagens für die spektrophotometrische Bestimmung von Aluminium.

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Buchbesprechungen

Gmelins Handbuch der anorganischen Chemie, 8. Auflage, *Sauerstoff (Lieferung 4) System Nr. 3*, 1960, xv+366 Seiten, 76 Figuren, Verlag Chemie G.m.b.H. Weinheim/Bergstrasse, Kartoniert DM 223,—.

Die Lieferung 4 zum Band *Sauerstoff* umfasst die Kapitel Luft, aktiver Sauerstoff und Ozon unter Berücksichtigung der Literatur bis Ende 1949. Im Kapitel Luft sind in diesem Band lediglich die physikalischen Eigenschaften beschrieben. Das chemische Verhalten ist in den Bänden der jeweiligen Reaktionspartner zu finden.

Nach einem Überblick über die Zusammensetzung und Aggregatzustände der Luft folgt eine Beschreibung der mechanisch-thermischen, akustischen, optischen, magnetischen und elektrischen Eigenschaften unter besonderer Berücksichtigung der Zustandsgleichungen und des Joule-Thomson Effektes. Im Kapitel über aktiven (atomaren) Sauerstoff werden dessen Bildung und Darstellung, Nachleuchtspektrum und thermisches Verhalten behandelt. Der grösste Teil des Bandes befasst sich mit dem Ozon. Nach einem kurzen geschichtlichen Überblick folgt ein sehr ausführlicher Abschnitt über Bildung und Zerfall, worin zunächst die Gleichgewichte $3 O_2 \rightleftharpoons 2 O_3$ und $O_2 + O \rightleftharpoons O_3$ im thermischen und photochemischen Prozess sowie in elektrischen Entladungen in Sauerstoff und Luft beschrieben werden. Es folgen dann Abhandlungen über thermische und photochemische Bildung und Zerfall, über Bildung und Zerfall in elektrischen Entladungen (vor allem stille Entladung, Ozonapparate), bei Einwirkung von Ladungsträgern (Elektronen und α-Strahlen) sowie über die Bildung bei elektrolytischen und chemischen Vorgängen. Anschliessend werden die Methoden und Apparate zur Darstellung von Ozon im Laboratorium beschrieben unter Angabe der für maximale Ausbeuten erforderlichen Bedingungen (die technischen Verfahren sind bereits in der Lieferung 2 behandelt). Der Abschnitt über physikalische Eigenschaften befasst sich mit Fragen der Molekülstruktur, den mechanisch-thermischen, optischen, magnetischen und elektrischen Eigenschaften mit Daten neuerer Messungen. Im Abschnitt über das elektrochemische Verhalten werden das Normalpotential Einzelpotentiale und Ketten gegen Wasserstoff, Sauerstoff und Quecksilber behandelt.

Das Schlusskapitel des Bandes befasst sich mit dem chemischen Verhalten des Ozons
im allgemeinen, gegen Nichtmetalle, Metalle, anorganischen Stoffen, wobei in einem
besonderen Abschnitt die Reaktionen wässriger Ozonlösungen gegen Anionen und
Kationen beschrieben werden. Der letzte Teil dieses Abschnitts behandelt dann noch
einige organische Lösungsmittel für Ozon. Der Band ist mit Marginalien in englischer
Sprache versehen und enthält ein deutsch–englisches Inhaltsverzeichniss.

K. EDER (Genf

Gmelins Handbuch der anorganischen Chemie, 8. Auflage, *Strontium* (*Ergänzungsband*
System Nr. 29, 1960, iv, xxx, 306 Seiten, 39 Figuren, Verlag Chemie G.m.b.H.
Weinheim/Bergstrasse, Kartoniert DM 195.—, Ganzleinen DM 200.—.

Der Ergänzungsband zu dem 1931 erschienenen Band *Strontium* umfasst die For
schungsergebnisse von 1932 bis 1949. Ausser dem Element werden noch die Verbin
dungen des Strontiums mit den Nichtmetallen sowie mit den Metallen As, Sb, Bi
Be, Mg, Ca und Alkalimetale behandelt. Ungefähr ein Viertel des Bandes befass
sich mit dem Vorkommen des Strontiums, wobei neben den Lagerstätten auch da
Vorkommen in der Hydrosphäre und Biosphäre behandelt wird. Ferner wird auf di
Bedeutung der Strontium-Isotope für die geologische Alterbestimmung hingewiesen
Das Kapitel über die Technologie des Strontiums und seiner Verbindungen beschreib
die Verfahren zur Aufbereitung und den Aufschluss der Ausgangsmaterialien, di
technischen Darstellungsmethoden für das Strontiummetall und die wichtigsten Ver
bindungen mit Angaben über deren Verwendung. Im Kapittel über die Darstellung
des Elementes werden auch die Methoden zur Anreicherung und Abtrennung de
Strontium-Isotope besprochen. Ein Abschnitt über physiologische Schädigunger
weist auf die Gefahren im Umgang mit Strontiumverbindungen hin. Nach der Be
handlung der physikalischen Eigenschaften wird das elektrochemische und chemisch
Verhalten des Elementes bezw. Ions besprochen, wobei auch die analytischen Reak
tionen berücksichtigt wurden. Etwa die Hälfte des Bandes befasst sich mit den Ver
bindungen des Strontiums. Nach den Legierungen mit Ca folgen die Verbindunger
mit H, O, N, Halogen, S mit besonders ausführlicher Behandlung des Strontium
chlorids und -sulfates. Anschliessend werden die Verbindungen mit B, C, Si, P, As
Sb, Bi, Be, Mg, Ca und Alkalimetallen beschrieben. Der Band ist mit Marginalien
in englischer Sprache versehen und enthält ein deutsch–englisches Sachregister.

K. EDER (Genf

Polarographisches Praktikum par J. HEYROVSKÝ, Zweite neubearbeitete Auflage (An
leitungen für die chemische Laboratoriumspraxis, Band IV) vii + 116 Seiten, mi
105 Abbildungen. Springer Verlag, Berlin, 1960, 19.80 DM.

Remarquable ouvrage à double titre, d'abord parce qu'il présente en quelques 11

...ages, en un exposé clair et concis, l'une des plus étonnantes méthodes d'investigation ...e la science moderne, d'autre part parce que celui qui l'a écrit est le créateur de la ...éthode, ce qui lui a valu le prix Nobel de Chimie 1959.

Ce livre est destiné à tous ceux qui désirent pratiquer la polarographie et les mé-...hodes qui en découlent. Les explications en sont si simples et si complètes que chacun ...eut, sans aide extérieure appliquer cette méthode, même s'il n'a aucune connais-...ance du sujet.

Cet ouvrage comprend deux parties; la première traite de l'appareillage et des ...rocessus de mesure. La seconde décrit un certain nombre d'applications pratiques ...articulièrement bien choisies car elles permettent au néophyte de parfaire les con-...aissances acquises dans la première partie.

Le livre débute par une description des appareils, du plus simple qu'il est aisé de ...onstruire soi-même avec les moyens du bord — et l'auteur donne toutes précisions ... ce sujet — jusqu'aux polarographes enregistreurs. Les oscillographes et les dis-...ositifs à rayons cathodiques ne sont pas décrits, ils n'ont que faire dans un livre qui ...adresse plus particulièrement aux personnes non spécialisées. Il est aussi question ...'électrode à goutte de mercure, d'électrolytes de base, de sensibilité et de précision. ...es diverses cuves polarographiques macro et micro sont décrites ainsi que la tech-...ique d'essais des appareils, de la titration polarographique, etc.

Dans la seconde partie, l'auteur propose quelques applications, tant qualitatives ...ue quantitatives; il en profite pour décrire un certain nombre de phénomènes im-...ortants en polarographie tels que: effet de l'oxygène dissous et les moyens de s'en ...ébarrasser, les maximums et les suppresseurs de maximum; les courants cinétiques ...t leur interprétation. L'auteur décrit aussi quelques processus d'oxydation et de ré-...uction organiques et inorganiques, le problème des séparations et les déterminations ...icroanalytiques. L'ouvrage se termine par des tabelles de potentiels de dépolarisation.

Le tout est exposé en une progression régulière; à aucun moment l'auteur n'accu-...ule les difficultés, elles viennent les unes après les autres sans hâte, aussi s'initie-t-on ...ans peine à cette remarquable méthode. Il m'a très rarement été donné de lire un ...uvrage présentant de telles qualités didactiques.

D. MONNIER (Genève)

...ystematic Analysis of Surface-active Agents von MILTON J. ROSEN UND HENRY A. ...OLDSMITH, Interscience, New York, 1960, 422 Seiten, Preis: $13.50.

...n der Reihe der Monographien *Chemical Analysis* ist jetzt als Band 12 eine ausführ-...che Behandlung der systematischen Analyse oberflächenaktiver Substanzen er-...chienen. In einer kurzen Einleitung werden zunächst die verschiedenen Klassifizie-...ungsmöglichkeiten besprochen. Da die übliche Einteilung in anionen- und kationen-...ktive, nicht-ionogene und ampholytische Verbindungen für die chemische Analyse ...ieser Substanzen unpraktisch ist, wird dem beschriebenen Analysengang eine ...inteilung nach den vorhandenen Elementen zu Grunde gelegt: (*I*) enthält nur ...-H-O; (*II*) enthält C-H-O + Metall; (*III*) enthält C-H-O + S; usw. Im 2. Kapitel ...olgen dann Angaben über Nachweisreaktionen für oberflächenaktive Substanzen

(ohne Berücksichtigung der Zugehörigkeit zu den einzelnen Typen), über deren
Abtrennung von Begleitstoffen durch Extraktion, Austauscherharze oder Chromato-
graphie sowie quantitative Bestimmung nach Gruppen in Stoffgemischen. Das 3.
Kapitel befasst sich mit der qualitativen Analyse der oberflächenaktiven Substanzer,
wobei auch physikalische Methoden (IR und UV Absorption, Röntgenstrahlenbeu-
gung) berücksichtigt sind. Die chemischen Methoden erstrecken sich auf den Nachwei
der Elemente und funktionellen Gruppen. Der letzte Teil dieses Kapitels beschreibt
dann Methoden zur Identifizierung einzelner oberflächenaktiven Substanzen durc
Säurezahl, Jodzahl, Hydroxylzahl usw. Im 4. Kapitel werden die Methoden zu
quantitativen Bestimmung beschrieben, wobei ebenfalls die Gruppierung nach Ele
menten als Grundlage dient. Sehr ausführlich werden dann im 5. Kapitel die Methode
zur Trennung von Gemischen oberflächen-aktiver Substanzen behandelt. De
Anhang enthält eine Liste der bekanntesten im Handel (USA) befindlichen Surfac
tants mit Angaben über die chemische Zusammensetzung und deren Hersteller. I
einer zweiten Tabelle werden die Brechungsindices der wichtigsten Ausgangsprodukt
und einer Anzahl Fertigprodukte aufgeführt. Eine dritte Tabelle gibt Daten übe
Titer, SZ und JZ der Fettsäuren handelsüblicher Qualität mit Angaben über Zusam
mensetzung und Lieferanten. Sowohl die einzelnen Kapitel wie auch die Tabelle
sind durch zahlreiche Literaturreferenzen ergänzt.

Man muss den Autoren dankbar sein, dass sie es unternommen haben, die we
verstreuten Literaturangaben zu sichten und die besten Methoden in einem Buc
zusammen-zu-fassen und durch eigene Vorschriften zu ergänzen. Die Anordnung is
sehr glücklich gewählt, der Text kurz aber präzis und die Analysengänge sehr über
sichtlich durch die Anwendung des "Flowsheet" Prinzips. Das Buch ist vor allem fü
die Laboratoriumspraxis bestimmt und kann bestens empfohlen werden.

K. EDER (Gen

Anal. Chim. Acta, 24 (1961) 299–3

Announcement

CONGRESS FOR ANALYTICAL CHEMISTRY

A Congress on analytical chemistry will be held in Budapest, Hungary, from the 24t
to 29th April, 1961, under the auspices of the Hungarian Academy of Sciences an
with the patronage of the International Union of Pure and Applied Chemistry.

The Congress will deal with the following subjects: Theoretical basis of chemica
analysis; analytical applications of isotopes; complex chemistry and its analytica
application; organic analysis; electroanalytical methods; chromatography; spectro
chemical analysis; applied analysis. Plenary lectures will be given by Professors I. I
ALIMARIN (USSR), R. BELCHER (UK), G. CHARLOT (France), C. DUVAL (France), I
ERDEY (Hungary), L. GORDON (USA), J. HEYROVSKÝ (Czechoslovakia), K. JACIMIRS
KIJ (USSR), W. KEMULA (Poland), E. SCHULEK (Hungary), S. VEIBEL (Denmark
PHIL. W. WEST (USA), W. F. K. WYNNE-JONES (UK) and W. J. KIRSTEN (Sweden

Further information can be obtained from:

Magyar Kemikusok Egyesulete "Analitikai Kongresszus"
Budapest V, Szabadsag ter 17, Hungary.

PAPER ELECTROPHORESIS

A Review of Methods and Results

by **LUIZ P. RIBEIRO**
EMILIO MITIDIERI
OTTILIA R. AFFONSO

of the Biochemical Laboratory, Instituto Oswaldo Cruz,
Rio de Janeiro, Brazil

This book is a completely revised and enlarged translation of the very successful Portuguese edition of 1958.
The contents fall naturally into three sections:

a) Theoretical principles, techniques and apparatus
b) The determinations of proteins and the clinical applications
c) Studies of non-macromolecular substances such as vitamins, hormones, nucleic acid fragments, sugars, inorganic ions etc.

Major emphasis has been placed on paper electrophoresis although many related methods are critically reviewed. New techniques are described in detail and the many illustrations demonstrate the principles and applications discussed in the text. There is a comprehensive list of more than 3200 references.
The book should prove of great practical and theoretical value to all scientists concerned with natural processes.

6 x 9"   **viii + 441 pages**   **140 figures**   **42 tables**

CONTENTS:

Introduction
Theoretical Considerations
Methods and Apparatus
Protein Determination
Human Serum Proteins
Animal Serum Proteins
Other Studies of Proteins
Proteins in Other Biological Fluids
Haemoglobins
Lipoproteins and Related Subjects

Glycoproteins and Mucoproteins
Enzymes and Related Substances
Hormones and Related Substances
Vitamins and Related Compounds
Carbohydrates and Polyalcohols
Nucleic Acids and Their Constituents
Amino Acids and Peptides
Inorganic Substances
Immunochemistry and Related Studies
Other Applications

ELSEVIER PUBLISHING COMPANY
Amsterdam

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SPOT TESTS

in organic analysis

by FRITZ FEIGL, Eng., D.Sc., D.h.c.

Laboratório da Produção Mineral, Ministério da Agricultura, Rio de Janeiro (Brazil);
Professor at the University of Brazil;
Member of the Austrian and Brazilian Academies of Sciences

Translated by RALPH E. OESPER, Ph.D.

Professor Emeritus, University of Cincinnati

Sixth - completely revised and enlarged - edition

Ever since the publication of the 5th edition of this work on organic applications of spot tests, the author has continued his fundamental research in this field. This 6th edition is the proud result of the considerable new insight and knowledge acquired during the past four years, as evidenced by the following survey:

	Number of sections in	
	5th ed.	6th ed.
Preliminary (exploratory) tests	25	32
Tests for functional groups	49	70
Tests for individual compounds	78	133
Practical applications	62	111

As in the previous edition the abundant material, which deals with all theoretical and practical aspects of spot tests in organic analysis, is arranged in a compact and logical order. Nearly 600 tests, of which more than 200 are new, are described and the necessary information for each test is given, such as the practical details, limits of identification, known interferences and, whenever possible, the reactions underlying the test. As a token of the growing importance of spot test analysis Professor Feigl also describes successful and unique tests on synthetic fibres, plastics and rubbers, a field which has now been invaded in succession to the tests on pharmaceuticals, drugs, dyestuffs and examinations of purity described in the 5th edition and enlarged in this version.

The book serves three purposes. Analysts and other chemists will find a wealth of practical information on the increasingly important field of spot tests. Secondly, the book gives full information and valuable indications for further research to workers in the field of qualitative organic macro- and micro-analysis. Thirdly, the book has a high didactic value for students and teachers, since spot tests, which can be carried out with little trouble and expense, can contribute much to the knowledge and understanding of the reaction possibilities of organic compounds.

6 x 9"   xx + 675 pages   38 tables   32 illustrations   1960

LIST OF CONTENTS:

1. Development, Present State and Prospects of Organic Spot Test Analysis.
2. Spot Test Techniques (by Ph. W. West).
3. Preliminary (Exploratory) Tests.
4. Detection of Characteristic Functional Groups in Organic Compounds.
5. Identification of Individual Organic Compounds.
6. Application of Spot Reactions in the Testing of Materials, Examination of Purity, Characterization of Pharmaceutical Products, etc.

Tabular Summary of the Limits of Identification Attained by Spot Tests.
Author Index (approx. 1750 entries).
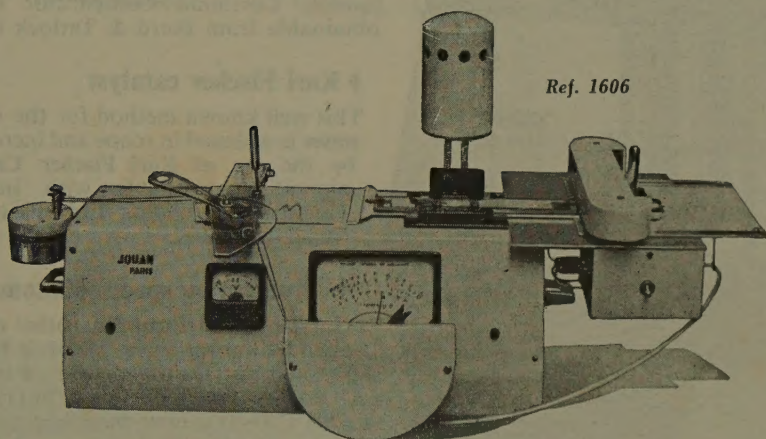Subject Index (approx. 6260 entries).